Effects of Metal Catalysed Peroxide Decomposition on the Bleaching of Mechanical Pulp

by

Douglas George Brown, B.Sc. (Hons.)

Submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

Department of Chemistry
University of Tasmania
September, 1993

This thesis contains no material which has been accepted for the award of any other higher degree or graduate diploma in any other tertiary institution, and to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text.

Abstract

Hydrogen peroxide is widely used as an industrial bleaching agent, particularly for the bleaching of mechanical pulps. Under the alkaline conditions required for effective bleaching a number of transition metal ions, including iron, copper and manganese, catalytically decompose peroxide resulting in a loss in the concentration of active bleaching reagent, with a subsequent reduction in the bleaching efficiency. In this study the effects of transition metal ions on the decomposition of hydrogen peroxide have been studied, both in the presence and absence of pulp. The influence of various additives, including sodium silicate and magnesium, on the rates of metal catalysed peroxide decomposition have also been studied.

The results of studies of the stability of alkaline hydrogen peroxide solutions in the absence of pulp have demonstrated that the behaviour of transition metal ions towards decomposition depends on the hydrolysis species of the metal present. Changes in the rate of decomposition over the course of the reaction can be attributed to changes in the catalytically active species present. The addition of a number of additives to peroxide solutions containing added transition metal ions can also lead to changes in the observed catalytic activity, either accelerating the rate of decomposition or stabilizing the systems. In the presence of these additives a correlation was observed between the catalytic activity of the transition metals and the formation of transition metal-additive complexes, which could be monitored by UV-visible spectroscopy. This implies that a direct interaction between the metal ions and additives is responsible for the observed changes in the catalytic activity. It is proposed that the mechanism by which the additives operate is by the formation mixed hydrolysis species with the transition metal ions, with the resulting species having altered catalytic properties.

Studies of the effects of metal catalysed decomposition in the presence of pulp were

conducted using a *P. radiata* TMP. The addition of the desired metal ions to pre-chelated pulp enabled their catalytic activities to be determined individually. The effects of sodium silicate and magnesium on the rates of metal catalysed decomposition were also determined in the presence of pulp. Comparison of the behaviour of these systems in the presence and absence of pulp reveals that the inclusion of pulp can have a significant influence on the catalytic activities. These results demonstrate that it is not possible to predict the peroxide decomposition behaviour during bleaching from studies conducted in the absence of pulp.

Dedication

This thesis is dedicated to my wife Melissa and my son Benjamin, for their constant love, support and unfailing trust. Without them this work would not have been possible.

Acknowledgements

I would like to express my sincere thanks to my supervisor, Dr. John Abbot, for the interest he has taken in this work and for the support and guidance that he offered. His dedication to duty, especially when severely inconvenienced with a back injury, was greatly appreciated.

To my fellow students, Graham, Kelvin, Ash, Felix, Phil, Karen, Rhitu, Vicky, Bimo, Zai and Yos, who provided a terrific atmosphere for both work and play, I offer my thanks, and look forward to maintaining the friendships that we have made for many years to come.

Thanks must also be extended to the entire staff of the chemistry department, both academic and technical, for their friendship as well as their contributions to this work.

To Darren and Yvonne, thanks for enduring many years of my partial presence and my fickle homemaking ways. Your friendship and support was greatly appreciated.

To my parents, thank you for the wonderful support you have provided over the years.

To Jim, Val and Ashley Manson, thank you for your "adoption" of me as your son and brother. You truly did gain a son instead of losing a daughter.

Finally, I must express my sincere gratitude to Australian Newsprint Mills Pty. Ltd. and Interox Chemicals Pty. Ltd. for their generous financial support of this work.

Table of Contents

CHAPTER 1

Literature Review
and
Research Proposal

1.1 Use of Hydrogen Peroxide in the Pulp and Paper Industry

Two general processes are commonly employed for the production of wood pulps, mechanical pulping and chemical pulping[1]. Mechanical pulping involves the use of physical force, such as grinding or refining with rotating discs, to separate the wood fibres[1]. This process has the advantage of producing high yield pulps, as essentially all of the wood components are retained[1]. However, as the lignin which contains the major colour forming components present in the wood is not removed during pulping, the resulting bleached pulps are of a relatively low brightness[2]. In contrast, chemical pulping results in the removal of the majority of the lignin giving higher bleached pulp brightnesses, but with lower yields[1]. Market requirements for both mechanical and chemical pulps necessitate their bleaching to produce pulps of appropriate final brightness. Hydrogen peroxide has been shown to be an effective reagent for the bleaching of both mechanical and chemical pulps[3-5].

Chlorine based chemicals such as Cl_2, ClO_2 and hypochlorite have traditionally formed the basis of sequences for the bleaching of chemical pulps. The effectiveness of these chemicals, together with the high cost of peroxide, has traditionally limited the use of hydrogen peroxide for the bleaching of chemical pulps[5-7]. However, recent environmental concerns have lead to an increase in demand for totally chlorine-free (TCF) and elemental chlorine-free (ECF) pulps resulting in the increased use of peroxide[3]. The active bleaching species for the delignification of chemical pulps by peroxide are thought to be hydroxyl radicals, perhydroxyl radicals and molecular oxygen, which are formed by peroxide decomposition[5,6]. This accounts for the observation that peroxide stabilizers generally have no effect, or a detrimental effect, on delignification[5].

The bleaching of the majority of mechanical pulps is carried out with either

hydrosulphite or peroxide[8]. Hydrosulphite bleaching is more cost effective than peroxide bleaching and is used extensively when low to medium brightness gains are required[8-11]. Peroxide bleaching is commonly used when higher brightness gains are required, and has the advantage of greater brightness stability[8-11]. Traditionally, hydrogen peroxide bleaching is carried out in towers under conditions of medium to high consistency, moderate temperatures (usually 40-70°C), alkaline conditions (initial pH 10.5-11.5), with retention times in the order of 1-2 hours[4,9]. The presence of alkali in the bleaching formulation facilitates the formation of the perhydroxyl anion which is thought to be the active bleaching species[4,12,13], as shown equation 1.1. Numerous other applications of peroxide have been reported including steep bleaching[14,15] (lower temperature and alkalinity, longer retention time), refiner bleaching[10,15,16], which takes advantage of the favourable conditions present during refining (high temperature, high consistency), and bleaching during flash drying[15,17] (very high temperature and consistency).

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H_2O \qquad \text{Eq. 1.1}$$

The decomposition of hydrogen peroxide is of great significance in the bleaching of mechanical pulps as it can lead to lower bleaching efficiency[18-23]. As a result, a great deal of effort has been focused on providing a greater understanding of the decomposition reactions involved, with a particular emphasis on the stabilization of peroxide[18-31]. Through the reduction of peroxide decomposition, the bleaching process can be made more cost efficient, resulting in either higher brightness gains or lower peroxide requirements.

1.2 Decomposition of Hydrogen Peroxide

The decomposition of hydrogen peroxide has been the subject of many studies reported in the literature, due to its importance in a wide range of fields including

biochemistry[32], organic synthesis[33] and numerous industrial applications[24,34-36]. Biological interest in the reaction stems from the discovery that the naturally occurring enzyme catalase effectively decomposes peroxide to water and oxygen, while another enzyme, peroxidase, utilizes peroxide in the oxidation of various organic substrates[32]. A wide range of model systems has been investigated in attempts to reproduce the catalytic behaviour exhibited by these naturally occurring enzymes[32,37-42]. The use of peroxide decomposition catalysts as an aid in synthetic organic chemistry followed the discovery by Fenton that the ferrous ion promoted the oxidation of malic acid by hydrogen peroxide[33,43]. It is widely believed that hydroxyl radicals formed by the decomposition of peroxide are the active oxidising species[33].

On an industrial scale, the decomposition of hydrogen peroxide is of importance in a number of different processes. For example, peroxide decomposition catalysts can be used to remove excess peroxide following the sterilization of food products[34], or to remove peroxide formed as an undesirable side reaction in fuel cells[35]. The decomposition of peroxide is also an important consideration in hydrometallurgical processes in which hydrogen peroxide is used as an oxidant[44].

The extensive use of hydrogen peroxide in the pulp and paper industry has necessitated a comprehensive understanding of its decomposition reactions. Unlike some other industrial processes where the removal of hydrogen peroxide is required, the decomposition of peroxide in bleaching formulations typically results in lower bleaching efficiency and is therefore undesirable[18-23]. The stabilization of peroxide under the conditions used for bleaching has consequently been studied in great detail in order to reduce the level of decomposition[18-31].

1.2.1 Alkali Induced Decomposition

The decomposition of hydrogen peroxide in aqueous alkaline solutions has been the

subject of many studies[24,45-53], with a wide range of often contradictory results reported. The reaction has been reported to follow zero[46,50], first[50] or second[45,49] order kinetics depending on the conditions used in these studies. Two general mechanisms have been proposed to account for the observed reaction; (1) spontaneous base catalysed decomposition[45,47,51] and (2) decomposition catalysed by metal ion impurities[29,49,50,52], with the latter receiving the majority of support. The wide variation in the reported results appears to be primarily due to the extreme sensitivity of the decomposition reaction to a number of factors including pH, water purity, source and purity of alkali, and reaction vessels used[24,48-50,52].

The effects of hydroxyl ion concentration on the rate of peroxide decomposition have been reported by a number of workers[24,45,47-50,52,53]. At low pH, high purity solutions of peroxide are reported to be stable[24]. However, as the pH is increased, the rate of decomposition increases to a maximum at about pH 11 and then decreases upon further addition of alkali[45,47,49,53]. Duke and Haas interpreted this observation in terms of a homogeneous base-catalysed decomposition mechanism[53], in which the role of the alkali is to produce singly ionised hydrogen peroxide, equation 1.1, which can then react with unionised peroxide to produce oxygen and water, equation 1.2.

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H_2O \qquad \text{Eq. 1.1}$$

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + OH^- \qquad \text{Eq. 1.2}$$

Using the rate expression shown in equation 1.3, the authors were able to explain the observed maximum in decomposition which occurred when the peroxide was ~50% ionised[53].

$$\frac{-d[H_2O_2]}{dt} = k[H_2O_2][HO_2^-] \qquad \text{Eq. 1.3}$$

The rate constant for the homogeneous base-catalysed decomposition obtained by Duke and Haas is shown in Table 1.1.

Table 1.1 : Rate Constants for the "spontaneous" base catalysed decomposition of hydrogen peroxide

Rate Constant $dm^3mol^{-1}s^{-1}$	Temperature (°C)	Year of Publication	Reference
$7.4x10^{-4}$	35	1961	Duke and Haas[45]
$\sim 7x10^{-6}$	35	1963	Koubek et al.[51]
$3x10^{-6}$	35	1983	Galbacs and Csanyi[49]
$5.6x10^{-7}$	30	1983	Csanyi et al.[47]
$4.7x10^{-7}$	35	1985	Evans and Upton[52]

Subsequent studies on the rate of base catalysed peroxide decomposition have shown that the reaction observed by Duke and Haas must have been catalytically driven to a large extent[51,52], as evidenced by the lower rate constants obtained in more recent studies, as shown in Table 1.1. The greater peroxide stability observed in recent studies can be attributed to improved purification techniques and the presence of more efficient chelating agents such as ethylenediaminetetraacetic acid (EDTA)[49,51], diethylenetriaminepentaacetic acid (DTPA)[53] and diethylenetriamine-NNN'N"N"-penta(methylphosphonic acid) (Dequest 2060)[52]. The ability to suppress peroxide decomposition to such a great extent using metal ion chelants has cast doubt on the validity of the base-catalysed mechanism. It is apparent that catalytic impurities play a major role in the decomposition reaction even under conditions of high purity[48-50,52]. Indeed, Evans and Upton who reported the lowest rate of spontaneous base-catalysed

peroxide decomposition still concluded that this probably represented a catalysed reaction[52].

The presence of catalytic levels of impurities has been used by a number of workers to explain the peroxide decomposition behaviour in aqueous alkaline solutions[24,49,50]. Trace levels of transition metal ions, generally believed to be the primary active catalytic species, have been shown to be present in commercial alkali sources[47,48], and may also be introduced in significant amounts through the water or peroxide[24,53]. The decomposition reaction has also been shown to be dependent on the nature of the reaction vessels used, indicating that these can also serve as a potential source of metal ion contamination[49,50].

Nicoll and Smith proposed that the increased rate of peroxide decomposition observed as the pH of the solution was increased was not due to the action of the hydroxyl ion itself, but rather to the formation of colloidal heavy metal hydroxides[24]. The metal hydroxides are reported to be particularly effective peroxide decomposition catalysts[24]. Further addition of alkali results in the re-dissolution of the metal hydroxide species with a resultant lowering of the peroxide decomposition rate[24]. Similar findings have been reported by Spalek et al., who also explained the effects of hydroxyl ions on peroxide decomposition in alkaline solutions in terms of the catalytic species present at given pH values[50]. Subsequent studies examining the effects of the addition of catalytic levels of transition metal ions have shown that a maximum rate of decomposition is found as the pH is increased[24,48,49,53]. The pH at which this maximum occurs was found to be dependent on the individual metals present, occurring at 9.5, 11.6, and 12.0 for manganese, iron and copper, respectively[49]. The presence of differing levels and forms of transition metal impurities can account for the wide range of findings obtained from various studies investigating the decomposition of hydrogen peroxide under alkaline conditions[24,49].

Alkaline solutions of hydrogen peroxide are commonly prepared as bleach liquors in the pulp and paper industry[19,24-30,53,54]. Decomposition of peroxide is obviously undesirable as it leads to a lower charge of the active bleaching reagent[27,29,53,54]. The addition of the chelating agent DTPA to the bleach liquor has been found to completely halt decomposition leading to the conclusion that the decomposition is a metal induced reaction under these conditions[53].

1.2.2 Metal Catalysed Peroxide Decomposition

The metal catalysed decomposition of hydrogen peroxide has been studied in great detail using an extensive range of catalytic species and reaction conditions. Metal catalysts investigated include platinum[55,56], palladium[55-57], gold[56], silver[56-58], osmium[59,60], cobalt[57,61,62], nickel[57,62], iron[63-66], copper[63,67-69] and manganese[27,35,70-72]. A variety of forms of these metal have been studied including addition as metal ions[27,63,65,66,69], complexed metal ions[37,39-41,73-75], supported metal ions[56,57,62], metal oxides[61,70,72,76-78] and supported metal oxides[35,38,79,80]. The form of the catalyst can have a significant bearing on the activity. For example, the activity of certain metals can be greatly enhanced by supporting them on a suitable substrate[35,56,62,81], while the chelation of metal ions can result in either enhanced or reduced catalytic activity[21,29,37,74,75,82].

The ability of metal catalyst systems to decompose peroxide has been reported to be closely linked to their individual electrochemical behaviour[38,39,41,57]. In order for a system to act as a decomposition catalyst it must exist in two oxidation states having a suitable redox potential such that the lower oxidation state can be oxidised by peroxide and the higher oxidation state reduced by it[61]. The redox potential has been shown to be a critical factor in determining the activity of a number of catalyst systems including metal ions in solution[38], supported metal ions[57], metal oxides[76] and supported metal oxides[80]. Similarly, the electronic structure of certain pure and doped metal oxide

systems has been related to their peroxide decomposition activity[78]. The reactivity of these oxides was found to increase in the order :

insulator < n-type semiconductor < p-type semiconductor[78].

While electronic considerations have been found to be important in determining the activity of metal catalysts, a number of other factors are also considered to be important. The activities of metal catalysts have been shown to be strongly dependent on the reaction conditions used such as temperature and pH[21,24,37,49,53,72]. The effects of pH in particular have been studied in considerable detail, with different metal ions found to behave differently as a function of pH[21,24,49,53] as shown in Figure 1.1. The dependence of the catalytic activity on the reaction conditions has been attributed to the occurrence of metal species with certain characteristics, such as oxidation potential and solubility, which effect their suitability to participate in oxidation-reduction reactions[21,24].

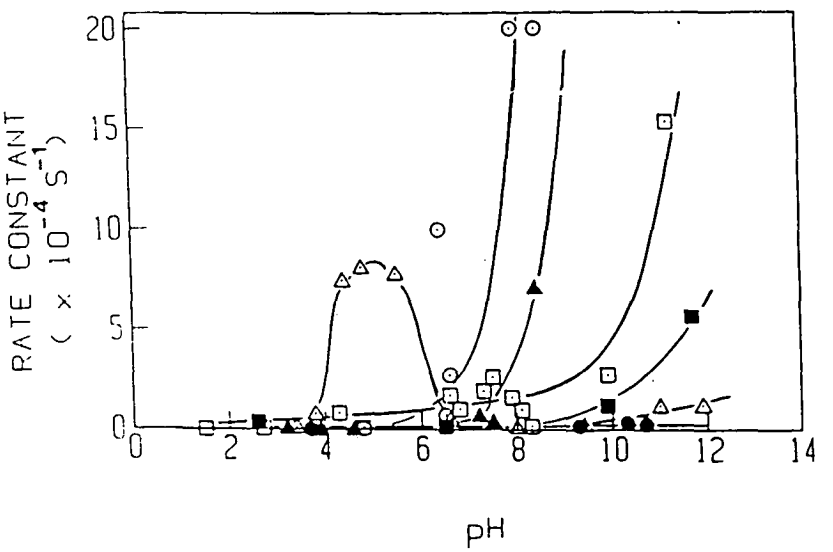

Figure 1.1 : Effect of pH on the peroxide decomposition catalysed by transition metal ions[21]. (Δ Cr(III) ; □ Cu(II) ; ○ Co(III) ; ▲ Mn(II) ; ● Ni(II) ; ■ Fe(III)).

The accessibility of hydrogen peroxide to the catalytic metal species has also been shown to be an important factor in determining the activity[37,74,75]. In a study of peroxide decomposition catalysed by copper(II) complexes, Sigel and co-workers reported a correlation between the catalytic activity and the number of free coordination positions on the metal[74,75]. Complexes containing bidentate ligands were found to be more active than those with terdentate ligands, while complexes with all four coordination positions of the copper engaged were found to be inactive[74,75].

Of the catalytically active transition metal ions iron, copper and manganese are generally considered to be of particular interest in the pulp and paper industry[18-22,29,53]. These metals are commonly present in peroxide bleaching formulations, being introduced from various sources including process waters, contact with machinery and as trace elements from the wood itself[18-22]. Under the alkaline conditions used, the presence of these metals can lead to significant levels of peroxide decomposition resulting in lower bleaching efficiency if not effectively controlled[18-21,29]. The importance of these species in peroxide bleaching processes warrants a closer investigation of the relevant literature.

1.2.2.1 Iron

The iron catalysed decomposition of hydrogen peroxide has been studied extensively under acidic conditions[63,65,66]. Studies conducted at low pH have predominantly stemmed from the discovery by Fenton[43] that a mixture of a ferrous salt and hydrogen peroxide possessed potent oxidising properties not present in the separate reagents[63]. Subsequent studies have interpreted the catalytic decomposition by iron in terms of a free radical mechanism or a complex mechanism. The free radical mechanism, first proposed by Haber and Weiss[64] and later modified by a number of workers, can be summarised as follows[83].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\cdot} \quad \text{Eq. 1.4}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^- \quad \text{Eq. 1.5}$$

$$HO^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad \text{Eq. 1.6}$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^+ + O_2 \quad \text{Eq. 1.7}$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^- \quad \text{Eq. 1.8}$$

$$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^- \quad \text{Eq. 1.9}$$

The complex mechanism proposed by Kremer assumes that complexes and compounds of iron and peroxide are intermediates in the reaction[83,84], as shown below.

$$Fe^{3+} + HO_2^- \rightarrow Fe^{3+}HO_2^- \quad \text{Eq. 1.10}$$

$$Fe^{3+}HO_2^- \rightarrow FeO^{3+} + OH^- \quad \text{Eq. 1.11}$$

$$FeO^{3+} + HO_2^- \rightarrow Fe^{3+} + O_2 + OH^- \quad \text{Eq. 1.12}$$

While numerous attempts have been made to distinguish between these two concepts there is still some doubt as to which mechanism actually operates[33,83].

In contrast to the large volume of work conducted under acidic conditions, there have been few investigations of iron catalysed decomposition under the alkaline conditions which prevail during peroxide bleaching. Iron, when present in low concentrations, has been found to stabilise alkaline peroxide solutions[7,24,53]. The only explanation given for this phenomenon is that peroxides or complex per-ions formed with iron are stable compositions[24].

At higher concentrations, iron has been shown to be an effective decomposition catalyst[24,53], with the addition of ferric or ferrous ions reported to give similar catalytic effects[85]. The catalytic activity in the presence of iron is closely related to the pH of the solution[24,49,53]. A maximum in activity has been reported to occur at pH 11.6[49],

while other studies found that the activity increased up to pH values of 11.8[53] and 12.0[24], the highest pH levels investigated in these studies[24,53]. Nicoll and Smith proposed that the increased activity observed on increasing the concentration of iron or the pH was due to the formation of ferric hydroxide[24]. The authors found that the addition of sodium chloride increased the amount of ferric hydroxide formed, resulting in increased peroxide decomposition[24]. Solutions obtained after the precipitated ferric hydroxide was removed by centrifuging exhibited much higher peroxide stability[24]. Hiskey also reports the high activity of freshly precipitated ferric hydroxide[44]. Ultrafiltration experiments conducted by Colodette and co-workers found that the iron was present in an insoluble form in alkaline solutions at pH 9.8, 10.8 and 11.8, indicating that the active catalytic species was an insoluble compound of iron[53].

Unlike the corresponding reaction under acidic conditions, little work has been reported on the mechanisms of iron induced peroxide decomposition under alkaline conditions. Isbell et al. proposed a free radical mechanism based on the results of studies conducted under acid conditions[85]. However, Colodette et al. found that the presence of iron actually reduced the measured amounts of hydroxyl and superoxide radicals, casting doubt on the validity of a free radical mechanism under alkaline conditions[53].

A number of studies have investigated the decomposition of peroxide catalysed by iron chelates under alkaline conditions. Chelation of iron by both DTPA[21,29] and EDTA[86,87] has been reported to produce more active catalytic species than iron alone. Detailed kinetic studies of the iron-EDTA system have established that the rate of catalysis is dependent on the complexed metal species present, with the monohydroxy complex $[Fe(edta)(OH)]^{2-}$ being the primary active catalyst[86]. However, these studies could not distinguish between free radical and complex mechanisms[86,87].

1.2.2.2 Copper

The decomposition of hydrogen peroxide by copper under alkaline conditions has been well researched[53,68,69]. The addition of peroxide to solutions containing copper results in the formation of a yellow-brown copper peroxide species which is an intermediate in the decomposition reaction[68,69,88]. The formation of this coloured intermediate species has been reported for systems containing copper ions[69,88], complexed copper[65,68] and copper supported on amphoteric oxides[81]. Luo and co-workers demonstrated the importance of this species in the decomposition reaction by a series of simple experiments using the chelating agent EDTA[69]. The addition of increasing levels of EDTA resulted in a suppression of the formation of the yellow coloured complex, together with a suppression of the peroxide decomposition[69]. Early attempts to identify the copper peroxide species led to the suggestion that the dimer $[HO_2\text{-}Cu\text{-}O_2\text{-}Cu\text{-}O_2H]$[89] or the monomer $[CuOO_2H]$[68] may represent the compound's formula. However, the recent study by Luo et al. identified the true structure as $[HO_2Cu(OH)_2^-]$ and presented the reaction mechanism which is summarised below[69].

$$Cu^{2+} + 3OH^- \rightleftharpoons Cu(OH)_3^- \qquad \text{Eq. 1.13}$$

$$Cu^{2+} + H_2O_2 + 3OH^- \rightleftharpoons HO_2Cu(OH)_2^- + H_2O \qquad \text{Eq. 1.14}$$

$$HO_2Cu(OH)_2^- \rightarrow Cu(OH)_2^- + HO_2^{\cdot} \qquad \text{Eq. 1.15}$$

$$Cu(OH)_2^- + H_2O_2 \rightarrow Cu(OH)_3^- + HO^{\cdot} \qquad \text{Eq. 1.16}$$

The production of both hydroxyl and superoxide radicals as a result of copper catalysed peroxide decomposition has been confirmed by the findings of many studies using a variety of radical detection techniques[48,53,90-94].

The relationship between the catalytic activity and the pH of copper/peroxide solutions has been widely studied. Galbacs and Csanyi reported a maximum rate of decomposition at pH 12 for high purity hydrogen peroxide solutions containing trace levels of added copper[49]. Nicoll and Smith found a similar maximum activity region at high pH and demonstrated that the position of the maximum is dependent on the concentration of copper present[24]. Luo et al. reported a zero-order dependence of the initial rate on the concentration of sodium hydroxide giving pH values of less than 12, while a first-order dependence was observed at higher pH's[69]. This study also reported a first-order dependence on the concentration of copper when peroxide is in excess[69].

1.2.2.3 Manganese

The manganese catalysed decomposition of hydrogen peroxide has been reported to be closely related to the manganese species present[7,21,27,53]. This is reflected in the complicated relationship between catalytic activity and pH observed for manganese[7,21,49,53]. A maximum in activity is observed at a pH of approximately 9.5-10.0, followed by a sharp decrease as the pH is raised to 10.5-11.0, with further increases in pH resulting in slightly higher rates of decomposition[7,49,53]. The formation of a number of insoluble manganese species including $Mn(OH)_2$, MnO, Mn_3O_4, MnOOH, Mn_2O_3 and MnO_2, together with soluble Mn(II) and Mn(III), as a function of alkalinity in aqueous solution in the absence of peroxide has been discussed in detail[95]. From the different oxidation potentials observed for various couples of these manganese species at different alkalinities[95] a strong correlation between the species present and the rate of peroxide decomposition may be expected.

The relationship between the solubility of the manganese species present and the decomposition of peroxide has been discussed by a number of workers[27,35,53,96-98]. Broughton and Wentworth reported that the addition of manganous salts to a peroxide

solution gave no decomposition until the addition of sufficient alkali to produce a brown colloidal precipitate[97]. Colodette et al. determined that manganese is essentially 100% insoluble at pH values of 9.8, 10.8 and 11.8 in the absence of peroxide and concluded that manganese dioxide is the most likely active species present[53]. Hartler et al. attributed the decrease in activity observed at pH 10.5 to the precipitation of manganese hydroxide[7]. However, the correlation between the solubility of the manganese species and the catalytic activity is complicated by the reported dissolution of solid manganese species in the presence of hydrogen peroxide[27,35]. The complete dissolution of the solid manganese species formed on the addition of alkali to manganese salts is reported to occur on the addition of peroxide[27,35].

Broughton and Wentworth reported a peroxide decomposition mechanism involving the reduction of colloidal manganese dioxide to soluble manganese hydroxide and the subsequent reoxidation, with hydrogen peroxide acting alternately as an oxidising and reducing agent[97]. In support of this mechanism experiments were conducted with radioactively labelled manganese initially present either 100% in solution or 100% in colloidal form[97]. Examination of the radioactively labelled manganese following reaction with hydrogen peroxide revealed an even distribution between the resulting colloid and the solution[97]. The mechanism given is shown below.

$$MnO_2 + H_2O_2 + 2H^+ \rightarrow Mn^{2+} + 2H_2O + O_2 \qquad \text{Eq. 1.17}$$

$$Mn^{2+} + 2H_2O_2 \rightleftharpoons Mn(OH)_2 + 2H^+ \qquad \text{Eq. 1.18}$$

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2H_2O \qquad \text{Eq. 1.19}$$

Subsequent studies on the manganese dioxide catalysed decomposition of peroxide have demonstrated a correlation between the level of surface excess oxygen, indicating the presence of Mn^{3+} centres, and the catalytic activity[72,99,100]. This led to the conclusion that the decomposition occurs through the Mn^{4+}/Mn^{3+} couple[72,99]. The decomposition has been reported to be entirely heterogeneous[70], with both first and

second order kinetics found under certain conditions[99]. Baral and co-workers found the reaction between manganese dioxide and peroxide to be autocatalytic[101]. Activation of the manganese dioxide was reported to occur through the formation of Mn^{3+} centres, while the addition of Mn^{2+} ions could also activate the catalyst[101]. The authors proposed the following mechanism, where the accumulation of Mn^{3+} centres accounts for the observed autocatalysis[101].

$$Mn^{4+} + H_2O_2 \rightarrow Mn^{3+} + 2H^+ + O_2^{\cdot-} \qquad \text{Eq. 1.20}$$

$$Mn^{3+} + H_2O_2 \rightarrow Mn^{2+} + 2H^+ + O_2^{\cdot-} \qquad \text{Eq. 1.21}$$

$$Mn^{2+} + Mn^{4+} \rightarrow 2Mn^{3+} \qquad \text{Eq. 1.22}$$

$$Mn^{2+} + H_2O_2 \rightarrow Mn^{4+} + 2OH^- \qquad \text{Eq. 1.23}$$

$$O_2^{\cdot-} + H_2O_2 \rightarrow O_2 + OH^{\cdot} + OH^- \qquad \text{Eq. 1.24}$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + O_2^{\cdot-} + H^+ \qquad \text{Eq. 1.25}$$

1.2.3 Formation of Radicals

While the formation of radical species is well established during the catalytic decomposition of hydrogen peroxide under acidic conditions[33,63,64], there appears to be confusion over the involvement of these species under alkaline conditions. Much of the evidence for the formation of radicals under alkaline conditions appears to be derived from comparisons with the analogous systems under acidic conditions[85], or from indirect evidence from reactions with various organic compounds which have been attributed to radical species[102,103]. Peroxide decomposition catalysed by a range of transition metals including iron, copper and manganese under alkaline conditions has been attributed to free radical mechanisms in this way[85,102,103].

A recent study conducted under alkaline conditions by Colodette et al. using esr to detect hydroxyl and superoxide anion radicals reported that, while the presence of

copper resulted in increased levels of radical species, the presence of iron and manganese did not[53]. The formation of radicals during the copper catalysed decomposition of alkaline hydrogen peroxide has been confirmed by a number of workers[90-93]. Similarly, the predominant mechanism for iron catalysed peroxide decomposition under alkaline conditions has been shown not to involve the generation of free radicals[90,92,93]. However, in the case of manganese, opinion is divided over the mechanism which operates, with support for both a radical mechanism[104] and a mechanism which does not involve the formation of radical species[90,92,93]. A recent study by Hobbs and Abbot using the specific hydroxyl radical trap DMNA has demonstrated that, while low levels of manganese do not increase the production of radicals, the addition of high levels of manganese results in a significant increase in the formation of hydroxyl radicals[90].

1.2.4 Stabilization of Hydrogen Peroxide

The decomposition of hydrogen peroxide under the alkaline conditions which prevail in typical bleaching liquors is considered to be undesirable as it leads to lower bleaching efficiency[18-23]. Consequently, a large number of studies have investigated the effects of various additives on the reduction of the level of decomposition[18-31]. Many attempts have been made to determine the mechanisms involved in the stabilization processes, with a wide range of proposals gaining varying degrees of support. The three most common stabilizing agents used for the control of decomposition in peroxide bleaching systems are chelating agents, sodium silicate and magnesium salts[9,23-28]. The effects of these additives, used both individually and in combination, have been studied in considerable detail providing a good basis for the understanding of the processes involved in stabilization[9,23-28].

1.2.4.1 Chelating Agents

The primary role of chelating agents in peroxide bleaching processes is the complexation and subsequent removal of catalytic metal ions prior to the addition of peroxide[2,9,18,105,106]. However, the formation of metal chelant complexes in alkaline peroxide solutions has also been shown to result in modifications in the catalytic activity towards decomposition[21,37,86,87]. The chelation of metal ions can result in either the stabilization or acceleration of decomposition depending on the combination of metal and chelating agent used[21,41].

The use of chelating agents to enhance the catalytic activity of copper has been studied extensively in attempts to model the enzymatic properties of catalase and peroxidase[37]. Sharma and Schubert have attributed increased catalytic activity to modifications in the redox potential on complexation[41]. These workers state that the redox potentials of copper complexes having two nitrogen donors are optimum for a one-electron transfer from the peroxide anion to the central copper ion[41]. Catalase type activity has also been reported for complexes containing iron and manganese[82].

The chelation of metal ions does not always result in increased catalytic activity. Sigel and co-workers report that the saturation of the coordination sites of the metal results in the inactivity of the complex[37,74,75]. Bambrick attributed the stabilization observed on the chelation of metal ions to the prevention of interactions between the peroxide and the metal centre[29]. An alternative explanation for the stabilization of decomposition is the formation of less active catalytic species by chelation than would otherwise be present[45].

A number of studies have reported the effects of chelating agents commonly used in the pulp and paper industry[21,29,46,53]. In the near absence of transition metal ions, both EDTA[49] and DTPA[53] can provide almost total stabilization of alkaline peroxide

solutions. The effects of commonly used chelating agents in the presence of transition metal ions have also been studied, with behaviour found to be dependent on the individual metals present[21,29]. Burton and Campbell reported that the addition of the chelating agents DTPA or DTMPA to alkaline peroxide solutions containing added copper or manganese resulted in stabilization whereas an accelerated rate of decomposition was observed in the presence of iron[21].

1.2.4.2 Sodium Silicate

The stabilization of hydrogen peroxide is one of the major roles attributed to sodium silicate during the bleaching of pulp[21,25,30,31,107]. As a result, the effects of silicate on the decomposition of peroxide in alkaline solutions have been studied in considerable detail[7,24,25,27,30,31]. A number of proposals put forward to explain the peroxide decomposition behaviour in the presence of silicate involve the interaction of silicate with either transition metals[24,25,27], hydrogen peroxide[7,108] or radical species[102,109]. Of these theories the former has received the majority of support. However, opinions vary as to the exact nature of the interaction between the silicate and the transition metal species[24,25,27].

The addition of sodium silicate to alkaline peroxide solutions in the absence of added transition metal ions has been reported to produce stabilization over a wide pH range[19]. The effect of silicate dose as a function of pH has been studied by Hartler et al., with silicate found to give reasonable stabilization up to a certain pH, but extremely poor stabilization at higher pH levels[7]. Increasing the silicate level resulted in an increase in the maximum pH at which stabilization occurred[7] as shown in Figure 1.2. Studies by Nicoll and Smith[24], and more recently Colodette et al.[25], found that rather than stabilizing peroxide, increased decomposition occurred at higher pH in the presence of silicate, implying that silicate by itself cannot be considered to be a stabilizer. Nicoll and Smith observed a dependence of the behaviour on the purity of

the make-up water used, suggesting that the trace metals present have a significant influence on the effect of silicate[24].

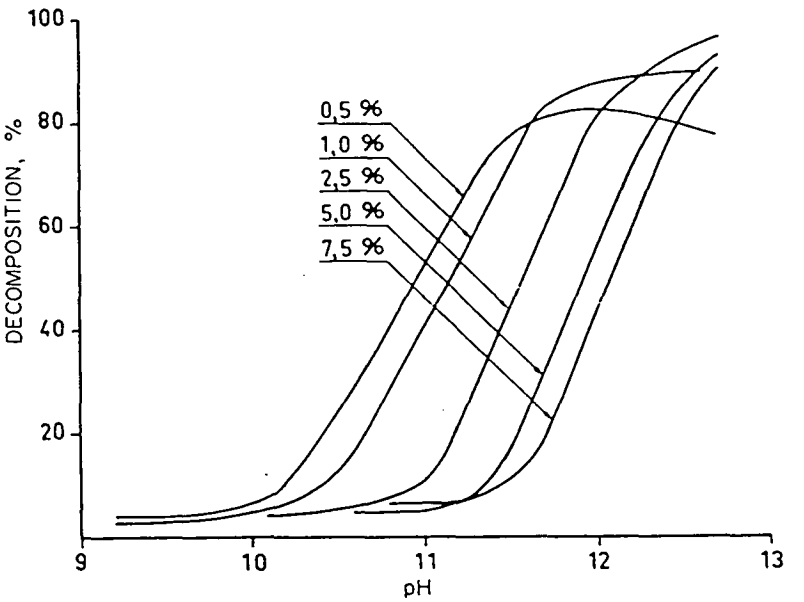

Figure 1.2 : Effects of silicate dose on the decomposition of alkaline hydrogen peroxide as a function of pH[7].

The effects of the addition of sodium silicate to alkaline peroxide solutions containing added transition metal ions have been studied by a number of workers[21,24,25,27]. In the presence of manganese, silicate has been reported to act as a stabilizer, producing significant reductions in peroxide decomposition[21,25,27]. In contrast, the addition of silicate to solutions containing copper reportedly leads to increased peroxide decomposition[21,24,25]. Some doubt exists about the action of silicate in the presence of iron. Burton reports a slight increase in peroxide decomposition on the addition of silicate to a solution containing iron[21], while Colodette et al. found that silicate acted as a stabilizer in the presence of either fresh or aged iron[25].

The mechanism by which silicate operates has been discussed in detail in the literature. Evidence from both e.p.r. studies[109] and reactions with organic compounds[102] have

led to suggestions that silicate ions may act as radical scavengers, thus providing stabilization by interrupting chain reactions. However, Colodette et al. examined the effects of silicate on the level of radicals produced in the presence of copper and found no significant decrease in the concentration of hydroxyl or superoxide anion radicals, concluding that silicate does not act as a radical scavenger[25].

The action of sodium silicate on the transition metal ion catalysed decomposition of peroxide has been attributed to its ability to form stable complexes with the metal species[24,27]. Abbot reports a correlation between the absorbance of peroxide solutions containing manganese and the catalytic activity for different levels of silicate addition[27]. The change in absorbance is said to relate to the manganese species present, with the formation of mixed binuclear hydrolysis complexes containing structural units of the type Si-O-Mn proposed[27]. Nicoll and Smith claim that the complexation by silicate results in a solubilization of the transition metal ions, thus preventing the formation of insoluble metal hydroxide species that are thought to be active catalytic species[24]. Colodette et al. studied the solubility of aged metal species in the absence of peroxide and found that the addition of silicate did not lead to any solubilization[25]. However, the addition of silicate did result in stabilization of peroxide in solutions containing iron or manganese regardless of the prior aging of the metals, indicating that silicate can deactivate solid forms of the transition metal catalysts[25].

The colloidal properties of sodium silicate have also been linked with its ability to prevent the decomposition of peroxide[24]. The inhibiting action of colloids reportedly stems from their ability to adsorb or absorb catalytic ions thus preventing the initiation of the peroxide decomposition reaction[24]. However, studies using a wide range of organic colloids have failed to establish any as effective stabilizing agents, resulting in the importance of the colloidal properties of silicate on its ability to stabilize peroxide being questioned[24,25].

1.2.4.3 Magnesium

The stabilizing effects of magnesium salts on peroxide bleaching liquors are well known, with small doses capable of almost completely retarding decomposition reactions[4,26,28]. Epsom salt, magnesium sulfate, enjoys widespread use as a bleach liquor stabilizer, particularly when the liquor is stored prior to use[4,28]. Many studies have also reported the effects of magnesium on the catalytic activity of various transition metal ions in alkaline peroxide solutions[24,26,27]. Magnesium has been found to stabilize peroxide in solutions containing iron or copper[26], while accelerating the rate of decomposition in the presence of manganese[26,27] and silver[24].

Two general mechanisms have been proposed to explain the effects of magnesium on peroxide decomposition. The formation of stable complexes between the magnesium and certain peroxide or free radical species has been discussed in relation to the protection of cellulose by magnesium during oxygen bleaching, where the stabilization of peroxide is thought to be important[110-112]. Isbell and Frush proposed a mechanism involving the formation of a magnesium superoxide complex in conjunction with their work on the degradation of carbohydrates[113]. The formation of a stable magnesium superoxide complex has also been proposed to explain the stabilization of alkaline hydrogen peroxide by magnesium[26], as shown in equation 1.26. The formation of such a complex can explain an increase in superoxide anion radicals detected in the presence of magnesium, while the slower decomposition of the magnesium superoxide complex accounts for the gradual decline in the level of these radicals detected with time[26], equation 1.27.

$$2O_2^- + Mg^{2+} \rightarrow Mg(O_2)_2 \qquad \text{Eq. 1.26}$$

$$Mg(O_2)_2 \rightarrow MgO_2 + O_2 \qquad \text{Eq. 1.27}$$

Despite e.s.r. evidence supporting the existence of a magnesium superoxide complex[113], the role of magnesium as a radical scavenger has been considered improbable[110]. A polarographic study by Sinkey and Thompson determined that magnesium did not interact directly with the peroxide molecule, but rather an interaction between the magnesium and catalytic metal ions was responsible for peroxide stabilization[114]. A similar study by Gilbert et al. also concluded that in the presence of gluconic acid the formation of soluble complexes between magnesium and either iron or copper was responsible for the stabilization of peroxide[115]. In addition, Abbot points out that the formation of stable complexes between magnesium and radical species cannot account for the accelerated rate of peroxide decomposition observed on the addition of magnesium to solutions containing manganese, suggesting instead that the formation of complexes between magnesium and transition metals can influence the catalytic activity by altering the redox cycle of the metal catalysts[27].

While magnesium has been shown to affect the catalytic decomposition of hydrogen peroxide through its interaction with transition metal ions, the exact nature of the interaction is not certain. Gilbert et al. suggested the formation of soluble complexes in the presence of gluconic acid, with hydroxo (-OH-) or oxo (-O-) bridges between the magnesium and the metal centres[115]. The formation of a complex of this type was also proposed by Abbot for the interaction between magnesium and manganese in alkaline peroxide solutions[27]. Nicoll and Smith reported that the removal of precipitated magnesium hydroxide from peroxide solutions containing copper resulted in increased stability, implying that an interaction existed between the copper and the insoluble magnesium hydroxide[24]. The adsorption of metal ions by magnesium hydroxide resulting in the stabilization of peroxide has been reported by a number of workers[46,116].

The accelerated level of peroxide decomposition in the presence of silver oxide observed on the addition of magnesium hydroxide has been attributed to the insoluble

hydroxide acting as a support for the silver oxide[24]. Similarly, Razouk and co-workers found that the impregnation of solid magnesium hydroxide with manganese produced a much more active decomposition catalyst than manganese alone[35]. In contrast, a catalyst prepared by the co-precipitation of manganese and magnesium hydroxide had a much lower activity than the catalyst prepared by impregnation, which was attributed to the decrease in the surface concentration of manganese available to react with peroxide[35]. The co-precipitation of transition metal ions with magnesium hydroxide has been reported by other workers to be an effective method of peroxide stabilization[47].

In peroxide bleaching formulations, magnesium salts are widely used in conjunction with sodium silicate[9,18,19,26]. Under these conditions the formation of colloidal magnesium silicate is reported to occur, with the resulting species being a particularly effective stabilizing agent[9,18,29,54]. Stabilization by magnesium silicate is reported to occur through the adsorption of metal ion catalysts[18,29].

1.3 Hydrogen Peroxide Bleaching of Mechanical Pulps

The production of pulp using mechanical techniques provides efficient use of wood resources, energy and chemicals[2]. The retention of not only the carbohydrate component of the wood, but also the lignin and extraneous components, give mechanical pulps their high yield characteristics with the subsequent advantage of obtaining more paper from a given quantity of raw material[1,2]. However, as the colour of the wood is derived primarily from the lignin and extraneous components, the resulting pulps are of low brightness and require bleaching[2,9].

The bleaching of mechanical pulps requires the modification of the coloured structures present, without a reduction in the yield[9]. Two types of bleaching agents are commonly used; reducing agents (e.g. hydrosulphite, borohydride) and oxidizing

agents (e.g. peroxide, hypochlorite)[9]. Of these bleaching agents, hydrosulphite is used most widely, while hydrogen peroxide is also used, particularly for bleaching to high brightness[8,9]. The use of hydrogen peroxide has traditionally been limited by its high cost[9]. However, recent environmental concerns about the use of chlorine based bleaching agents have led to its increasing popularity[3]. Hydrogen peroxide bleaching of mechanical pulps is also reported to have the added advantage of improving the strength and surface properties[117].

Numerous studies have been reported investigating various aspects of the bleaching of mechanical pulps with hydrogen peroxide[4,10,18,23,118,119]. The bleaching process has been shown to be extremely complex, with a large number of variables capable of having a significant effect on the bleaching response[4,18,23,118]. Factors that have been shown to influence peroxide bleaching include the wood source, pulping technique, pulp age and bleaching parameters[4,18,23,118]. In order to gain a greater understanding of the complexities involved in the peroxide bleaching process it is advantageous to consider these factors in more detail.

1.3.1 Variables in Raw Materials

The brightness responses of pulp samples bleached with hydrogen peroxide have been shown to be dependent on the wood species used[4,23,118,120,121]. Pulps prepared from spruce, balsam fir, Douglas fir, basswood and birch have been shown to respond favourably to peroxide bleaching[4]. However, for both softwoods and hardwoods, the bleaching response may vary depending on the species used[23,120,121]. In addition, it has been reported that bleachability of a given species can vary from area to area and from tree to tree[118].

The age of trees used has been reported to be another factor which can influence the bleachability of pulps[23,122-124]. Generally pulps produced from younger trees

respond better to bleaching than those produced from older trees[23,122-124]. This effect has been attributed to chemical changes which occur as the trees age[23,122,124]. Studies have also established that bleachability of pulps produced from different sections of trees may be different[124,125]. Heartwood is reported to give a particularly dark pulp which is difficult to bleach to high brightness levels[124]. The age of the pulp prior to bleaching has also been reported to influence the response[4,118]. Immediate bleaching following pulping is reported to give the best brightness responses[4,118].

The presence of extraneous materials introduced with the wood species is thought to have a direct influence on the bleaching behaviour[4,23]. The proportion of bark which is pulped with the wood is reported to affect the bleaching response, with high levels of bark leading to lower brightness gains[23,126]. The level of metal ions present in the pulp is also generally considered to directly influence the bleaching response[4,9,18,19]. Transition metal ions, present as naturally occurring constituents of the wood, are retained in the pulp and are reported to lead to poorer bleaching responses through the decomposition of peroxide[4,9,18,19]. Decay in wood may also result in increased peroxide decomposition due to the presence of bacteria and enzymes which are thought to be powerful catalysts[4,23].

1.3.2 Pulping Variables

The brightness of pulps can vary significantly depending on the method of pulping and the conditions employed, which in turn can have a major bearing on the final brightness achieved after bleaching[23]. This was demonstrated in a recent study which found that the brightness of *Pinus radiata* thermomechanical pulps produced by a number of Australian mills differed significantly, while pulps produced in a pilot plant using the same wood samples were of a similar brightness level[122]. Factors such as temperature, pretreatment, retention time in pretreatment, refiner pressure and retention time in refining have been reported to affect the brightness of pulps[23].

Pulping processes are widely believed to be an important source of transition metal ion impurities which can lead to peroxide decomposition in subsequent bleaching reactions resulting in decreased efficiency[18,19,22,118]. Transition metals may be picked up during pulping either through the mill waters, pulping chemicals or contact with machinery[18,19,22,118]. The temperature during pulping can influence the form of the metals, particularly iron, and the residence time is reported to affect the degree of colour formation caused by metal ions[2,127]. Treatments to decrease the metal content prior to pulping, or to reduce the effects of the metals present, can result in pulps of higher brightness being obtained[2,23,106].

1.3.3 Bleaching Variables

The conditions employed during the peroxide bleaching of mechanical pulps are of great importance in determining the bleaching response obtained[4,9,23]. The primary bleaching variables are peroxide charge, pulp consistency, alkalinity, temperature and retention time[4,9,23]. The first two variables control the amount of peroxide in contact with the pulp, while the last three are interdependent and can be adjusted within limits without altering the overall bleaching effect[4,9]. In addition to these variables, the levels of various transition metals present also has a major bearing on the bleaching response (see section 1.3.4).

1.3.3.1 Peroxide Charge

Numerous studies have established that increased peroxide charges result in increased brightness gains together with increased peroxide consumption[4,9,23]. The increases in brightness are reported to become progressively smaller as higher levels of peroxide are used[23]. Economic considerations have traditionally limited the level of peroxide used in industrial bleaching processes[4,9]. However, recent studies have suggested that the use of very high peroxide levels may be feasible, providing the residual peroxide

can be effectively utilized[128].

1.3.3.2 Pulp Consistency

High pulp consistencies have been shown by many workers to be favourable for peroxide bleaching[4,10,12,15,23,129-132]. This effect has been attributed to increases in the bleaching ability of the peroxide[133]. At high consistencies the peroxide concentration is greater for a given peroxide charge and a higher proportion of the peroxide is expected to be inside the fibre wall and thus available for bleaching[23,130,131]. An alternative explanation for the increased bleaching response at higher consistencies is the reduction of unfavourable peroxide consuming reactions[107,134]. Ali et al. suggest that the effect is due to the effective chelation of metal ion decomposition catalysts by the pulp at high consistencies[107], while Hagglund and Lindstrom suggest that the increased dewatering necessary to produce high consistency pulps results in less carry over of dissolved substances and heavy metals into the bleaching process[134].

1.3.3.3 Alkalinity

Alkalinity is an extremely important parameter in the peroxide bleaching of mechanical pulps[12,15,23,107,131,133,135-139]. The primary role of the alkali is to facilitate the generation of perhydroxyl anions, which are widely accepted to be the active bleaching species[12,15,23,131,133,136,137,139]. However, high levels of hydroxide ions also promote chromophore creation reactions, ie. alkali darkening[12,23,133,139-142], and also favour peroxide decomposition reactions[15,21,23,136,137,139]. As a result an optimum alkalinity exists where the brightening reactions are maximised and the chromophore creation and decomposition reactions are minimised[131,133,136,139]. An example of this effect is shown in Figure 1.3.

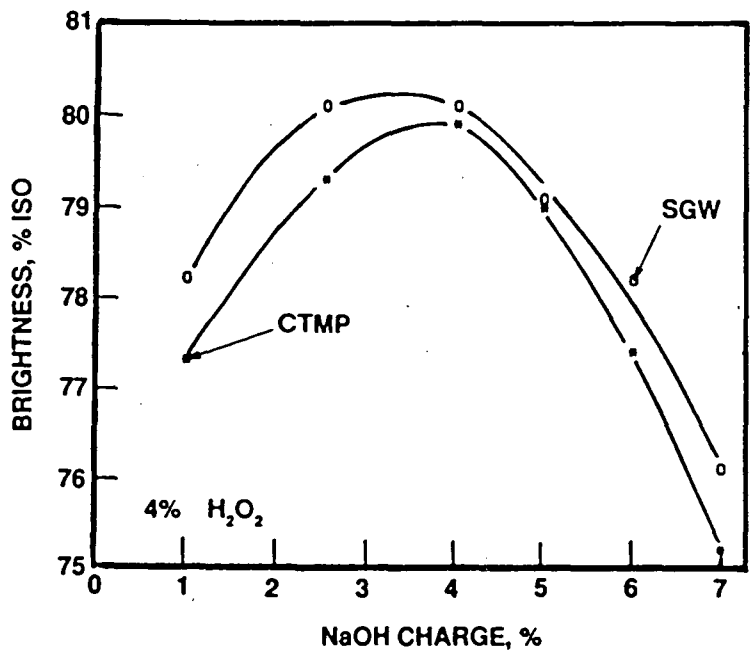

Figure 1.3 : Effect of NaOH charge on the bleaching of mechanical pulps[136].

The optimum alkalinity may be influenced by a number of factors[12,23,138,139]. The pH generally drops during the course of bleaching reactions due to the consumption of alkali in reactions with wood acids formed during bleaching[10,138,143]. The level of peroxide decomposition can also affect the pH profile during bleaching, as peroxide decomposition results in increased pH[27,131]. The rate of the pH decrease over the course of bleaching is important in determining the optimum alkalinity[138,139]. The high initial alkalinity facilitates the bleaching reaction when the peroxide level is high, while towards the end of the bleaching reaction when the majority of the peroxide has been consumed, the decreased alkalinity reduces the extent of alkali darkening[138,139].

Excess hydrogen peroxide which remains if the pH drops below a level conducive for bleaching can be reactivated by the addition of further alkali, resulting in a higher overall brightness gain[136].

1.3.3.4 Temperature

The rate of peroxide bleaching has been shown by many workers to be dependent on temperature[4,17,23,131,135,144,145]. As a result a desired brightness gain can be reached in a shorter time by increasing the bleaching temperature[4,17,135]. In the range of 25-70°C, Moldenius reported that the increased bleaching rate observed at higher temperatures was matched by increased peroxide consumption, and concluded that bleaching temperature does not affect the bleaching stoichiometry[131]. However, in a study over a wider temperature range, 30-95°C, Liebergott et al. found that, in addition to increasing the bleaching rate at higher temperatures, additional brightness gains were obtained with lower levels of peroxide consumption[135] as shown in Figure 1.4. This behaviour suggests that at high temperatures the active peroxide bleaching component reacts rapidly with the pulp before its effectiveness is diminished by decomposition[135].

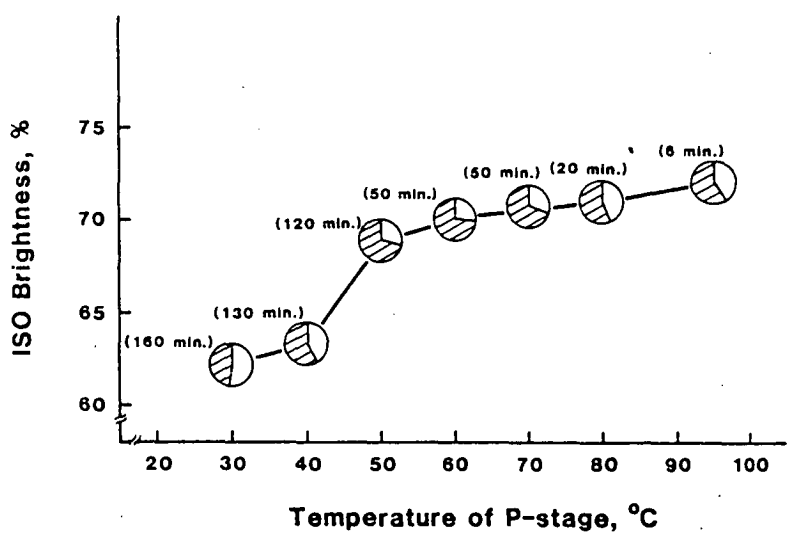

Figure 1.4 : Effect of temperature on the bleaching of a Spruce Balsam CTMP. (Time required for maximum brightness shown in brackets; peroxide consumption denoted by shaded areas in circles)[135].

1.3.3.5 Retention Time

The optimum retention time for peroxide bleaching is dependent on all of the previously discussed bleaching parameters[4,9,138]. If the retention time is too short then bleaching will not reach completion, resulting in less than optimum brightness gains and a waste of bleaching chemicals[4]. Conversely, if the retention time is too long alkali darkening reactions will result in lower brightness gains[138]. The retention time is commonly adjusted to compensate for changes in alkalinity or temperature[9,135]. A good example of this is the steep bleaching process, where the low temperature and alkalinity used necessitate a long retention time[14,15].

1.3.4 Effects of Transition Metal Ions

Transition metal ions, in particular iron, copper and manganese, have long been recognised as having deleterious effects on the peroxide bleaching of mechanical pulps[4,18,19,118]. These metals are thought to decompose peroxide under the alkaline conditions used during bleaching, leading to a lower available charge of the active bleaching agent[15,18-21,29,106,118,119]. The majority of evidence for the negative effects of metal ions has been based on the improved brightness responses obtained following the removal of the metals from the bleaching system[18,23]. However, a number of investigations have examined the effects of various forms of the metals directly by studying their addition to mechanical pulps[19-22,96,146,147].

A number of workers have determined that pulp is the major source of transition metal contamination, while mill waters and bleaching chemicals can also contribute to the overall level of metals present during bleaching[18,20,29,106,118]. The transition metal content of mechanical pulp is made up of naturally occurring constituents of the wood and impurities accumulated during the various stages of pulp processing[18,20,22,127]. Of the three major transition metals of interest, manganese is reported to originate

predominantly from the wood, while iron and copper have been found to accumulate during the processing of the pulp[18,22].

The form of transition metals in the presence of pulp has been related to their ability to catalytically decompose peroxide during bleaching[18,19,22]. Metal species may be expected to be chemically combined with various constituents of the wood[18,19,118]. Pulp components, or functional groups, have been reported to act as weak cation exchangers, where the metals exist in the form of a pulp-metal complex in equilibrium with free metal ions in solution[11,20]. Gupta and Mutton found that groundwood pulp had a strong affinity for trivalent metals like iron and aluminium, less affinity for divalent heavy metals and a very low affinity for the alkali and alkali earth metals[11]. The presence of metal-organic complexes in water insoluble form has been used to explain the difficulty in removing some metals by chelation[18]. Metals that are loosely complexed by the pulp and easily solubilized are thought to be active peroxide decomposition catalysts, while those which are strongly complexed, and hence not removed by chelation, are thought to be inactive[9,18,22].

Manganese is widely considered to be the predominant peroxide decomposition catalyst present during the bleaching of mechanical pulps[9,18,20,22]. Supporting evidence is provided by studies which indicate that manganese is present in the highest concentrations and is the most readily removed by chelation[9,18,22]. Studies investigating the effects of added metals on peroxide decomposition in the presence of bleached[96] and unbleached[20] pulps have also concluded that manganese is the most active of the catalysts studied. In contrast to manganese, the majority of the iron and copper present during the bleaching of mechanical pulps is reported to be tightly bound, ie. not removed by chelation, and thus inactive towards peroxide decomposition[18,22]. A study on the effects of the addition of aged iron and copper to α-cellulose derived from a Norway spruce TMP confirmed that strongly bound iron and copper are not catalysts for peroxide decomposition[22].

While the decomposition of peroxide is the primary role attributed to the transition metals present during bleaching, a number of studies have reported that these metals may also be involved in reactions leading to colour formation[2,20,96,140,148-150]. The addition of iron has been reported to have an adverse effect on the brightness of unbleached pulps[20,148] and on the rate of alkali darkening of pre-bleached pulps[96,140]. The addition of manganese has also been reported to lead to increased reversion for a pre-bleached pulp[140].

A study of the effects of added metals on the bleaching of groundwood pulp indicated that a decrease in bleaching efficiency, defined as brightness gain as a function of the amount of peroxide reacting with the pulp, occurred as the peroxide decomposition increased[21]. This effect was interpreted by Burton and Campbell to mean that the decomposition of hydrogen peroxide caused darkening of the pulp which was counteracted by bleaching reactions which consumed more peroxide, or that metal-catalysed reactions with the pulp consumed peroxide and caused the formation of chromophores resulting in reduced final brightness[21]. Pero and Dence reported that the addition of iron, copper or manganese to hydrogen peroxide solutions resulted in increased colour development in the presence of methoxyhydroquinone (MHQ), a component which has been identified in the spent bleach liquor from Norway spruce TMP[149]. The darkening reaction is presumed to occur through the reaction of MHQ with decomposition products of the peroxide[149]. This finding demonstrated the possibility of transition metals being involved in chromophore creation reactions[149].

1.3.4.1 Effects of Radicals

The role of peroxide radical species, in particular the hydroxyl and superoxide radical, in the delignification of chemical pulps has been investigated in a number of recent studies[151-153]. The hydroxyl radical is reported to be extremely reactive, and able to attack both lignin and cellulose rapidly[154]. Model compound studies have indicated

that a wide range of lignin structures is susceptible to attack by the hydroxyl radical[152,153,155,156]. The superoxide radical on the other hand is not believed to be an effective delignifying chemical during peroxide bleaching[157].

The generation of radical species is generally considered to occur via transition metal catalysed peroxide decomposition reactions[151]. Copper has been reported to be a particularly effective decomposition catalyst for the generation of radicals[53,90] while high levels of manganese have also been shown to result in increased concentrations of hydroxyl radicals in alkaline peroxide solutions[90]. As these metals are present in catalytic quantities in mechanical pulps, the formation of radicals is likely during peroxide bleaching processes[90].

Opinions are divided about the effects of radicals during the peroxide bleaching of mechanical pulps. Negative effects such as the degradation of lignin and colour reversion have been associated with the presence of radical species formed as a result of peroxide decomposition[96,158]. Radical species have also been reported to play a positive role in enhancing the effectiveness of peroxide bleaching[132,133,154]. The increased efficiency observed on bleaching at higher consistencies has been attributed to the action of radical species[133]. Work by Sjogren et al. using a displacement bleaching technique found that the rate of bleaching was higher in the latter stages despite the decreased levels of peroxide and alkali present[154]. This was interpreted as implying that highly reactive species, presumably radicals, are involved in the bleaching reaction[154]. Additional experiments involving the generation of hydroxyl and superoxide radicals by gamma irradiation demonstrated that these species can result in an increased bleaching rate[154]. A recent study by Hobbs and Abbot has questioned the beneficial effects of the radical species during the bleaching of mechanical pulps[90]. Using conditions of constant pH and peroxide, these workers found no improvement in bleaching after the inclusion of the transition metal catalysts copper and manganese, which were shown to result in an increased concentration of

hydroxyl radicals[90]. Similarly, the addition of stabilizers, which reduced the level of hydroxyl radicals, had no effect on peroxide bleaching under the conditions employed[90]. These workers concluded that the hydroxyl radical has little influence on the peroxide bleaching of mechanical pulps under typical conditions[90].

1.3.5 Stabilization of Peroxide During Bleaching

In an effort to counter the negative effects associated with hydrogen peroxide decomposition during bleaching, the stabilizing abilities of a wide range of chemicals have been tested in order to determine their suitability as additives[30]. Two main methods are commonly employed to reduce the extent of decomposition: the removal of transition metals prior to bleaching[2,18,106,119] and/or the deactivation of the metals present during bleaching[19,28-30,107]. Chelating agents are commonly used to perform the former task[2,18,106,119] while sodium silicate has been found to be the most effective of a wide range of chemicals in performing the latter role[18,28,30]. The effective use of stabilizing agents can have a significant positive effect on bleaching results, allowing either higher brightness gains to be obtained for a given peroxide charge[18,28,31,107], or a lower peroxide charge to be used to achieve a target brightness gain[31,107].

1.3.5.1 Chelating Agents

The use of chelating agents for the prevention of peroxide decomposition during industrial bleaching processes can be divided into two categories; the removal of metal ions by chelation and washing prior to bleaching[9,18,54,106,119], and the deactivation of metal ions by chelation during bleaching[23,29,31]. The principle role of chelating agents has been reported to be the control of manganese[106] while the addition of chelating agents prior to refining is reported to allow the control of iron prior to the formation of iron oxide[2]. A wide range of chelating agents have been tested as peroxide bleach

additives, with DTPA and EDTA being the preferred choice in the majority of industrial applications[2,23,29,106].

A number of factors have been reported to influence the effectiveness of the removal of metal ions by chelation including pulp washing efficiency, pH and aluminium content[105]. The importance of washing stems from the fact that chelated metal ions, while being less effective than free metal ions in decomposing peroxide, may still interfere with bleaching efficiency[105,134]. Indeed, Paasonen reported that if pulp was not washed, the addition of DTPA may have no effect, or even a deleterious effect[119]. However, the results of other workers contradict this finding, as chelating agents, including DTPA, were found to be effective when present during the bleaching process[23,31]. The variation in the reported effects of various chelating agents probably reflects the different pulps used, with different forms and contents of metal, and the different bleaching conditions employed in these studies[106].

The effect of pH on the efficiency of chelation is reported to be related to the relative stabilities of the pulp-metal and chelant-metal complexes[37]. The best results are reported to be obtained at pH values where the pulp-metal interactions are weak and the metal-chelant complexes are relatively stable[11]. The responses to chelation of individual metals present in pulp have been found to be different at various pH levels, reflecting their relative stabilities with various chelating agents[11]. These differences have been utilised for the selective removal of deleterious metals from chemical pulps, while retaining the majority of the magnesium and calcium which are expected to have stabilizing properties[159]. Similarly, the pH can be adjusted to allow the removal of manganese in the presence of aluminium[105]. Unless the correct pH is utilised the aluminium will be preferentially chelated, resulting in the inefficient removal of manganese and leading to lower bleaching responses[105].

1.3.5.2 Sodium Silicate

Sodium silicate has long been recognised as a valuable additive for the peroxide bleaching of mechanical pulps[4,118]. However, the exact functions performed by silicate during bleaching have been the topic of much discussion in the literature[28,30,107,160-164]. Early studies attributed the benefits obtained using silicate to its ability to perform in a number of roles including as a detergent, penetrant, buffer, stabilizer and corrosion inhibitor[4,118]. Silicate has also been reported to increase the bleaching ability of peroxide through the formation of peroxo-silicate species[108]. The importance of silicate as a peroxide stabilizing agent has become widely accepted[30,31,107]. However, the mechanism by which stabilization occurs remains a matter of conjecture (see section 1.2.4.2). The ability of silicate to perform in other roles and the relative importance of these functions remains the topic of much discussion[30,107,160-162].

Sodium silicate was found to be the most efficient of a large number of compounds tested by Kutney as peroxide stabilizers[30]. While a number of the compounds tested resulted in similar peroxide residuals, none gave the brightness gains achieved using sodium silicate, leading to the assumption that silicate may do more than prevent peroxide decomposition[30]. A study of the effects of chelation on the effectiveness of silicate during bleaching attributed approximately 50% of the benefit obtained to the deactivation of transition metal ions[107]. The beneficial effects observed for the bleaching of pre-chelated pulps implied that silicate must have at least one other role[107]. However, the results of a recent study cast doubt on the accuracy of this assumption, as the benefits of silicate are reported to be directly related to the efficiency of the chelation process[139]. The bleaching of a "superchelated" pulp was found to be unaffected by the presence of silicate, indicating that when transition metals are almost completely removed silicate addition has no additional beneficial effects to the brightness gain[139].

The role of silicate as a buffering agent during peroxide bleaching has been discussed in a number of recent publications[28,30,107,162]. Kutney examined the effect of silicate (4%) on the pH during the bleaching of groundwood pulp[30]. As no change was observed in either the initial or final pH values, or the pH profile during bleaching, it was concluded that silicate does not act as a buffer[30]. This finding is supported by the results of a study by Burton investigating a wider range of silicate additions[28]. It was found that a buffering effect only existed at the highest level of silicate addition (16%), and no effect was observed at lower silicate dosages[28]. However, the results obtained by Kutney have been re-interpreted by Ali et al. taking into consideration the different degrees of brightening observed in the presence and absence of silicate[107]. These authors point out that the primary reason for pH change during bleaching is the reaction of peroxide with lignin which consumes hydroxide ions[107]. Therefore, the increased brightness gain observed in the presence of silicate should result in a lower pH, and thus the silicate appears to act as a buffer[107]. A subsequent, detailed study into the role of silicate as a buffer established that when metals are not completely removed from the pulp the buffering effect of silicate results in higher brightness gains[162].

Sodium silicate has been reported to enhance the bleaching ability of hydrogen peroxide[4,30,108,118]. Early reports suggest that silicate acts as a penetrant, enhancing the interaction of the peroxide with the pulp fibres[4,118]. The formation of peroxo-silicate species, which are said to have enhanced bleaching ability, has also been proposed to account for the benefits observed in the presence of silicate[108]. However, a recent study by Graham et al. has established that silicate does not penetrate the fibre walls[161]. As the fibre wall brightens uniformly in peroxide bleaching, the validity of the proposed mechanisms involving increased penetration or an active peroxo-silicate species has been questioned[161]. A number of studies have investigated the activity of peroxysilicate directly, and while it has been shown that such species can form under bleaching conditions[165], they do not result in any improvements in the bleaching

response[28].

While the benefits of using silicate as a peroxide bleach additive are well documented, a number of negative effects have also been associated with its use[10,12,16,164,166]. Silicate has been reported to interfere with retention aid systems with a resulting negative effect on the retention of both fines and fillers[164,166]. In addition, the deposition of silicate has been reported to result in the fouling of equipment and/or paper machine wires and felts[12], while scaling on refiner plates is an undesirable side effect of its use during refiner bleaching[16]. The problems associated with silicate have led to a growing tendency to reduce or even eliminate its use in industrial applications using closed whitewater systems where the greater reuse of mill water can cause buildups of silicate[10].

1.3.5.3 Magnesium

The stabilizing effects of magnesium salts on peroxide bleaching liquors are well known, with small doses capable of almost completely retarding decomposition reactions[4,26,28]. However, in the absence of sodium silicate, magnesium is reported to have no effect on the bleaching of mechanical pulp[28,30,31]. This result apparently contradicts the earlier finding of Reichert et al. that the addition of Epsom salt could successfully control the metal catalysed decomposition of peroxide during bleaching[19]. However, a closer examination of the experimental conditions employed reveals that sodium silicate was included in the bleaching formulation[19]. Recent studies by Abbot and co-workers have demonstrated that the addition of magnesium salts can result in increased brightness gains in the absence of sodium silicate provided sufficiently high doses are employed[167].

The addition of magnesium to peroxide bleach formulations containing less than optimum levels of silicate has been reported to result in significantly increased

brightness gains[28,31]. When an optimum dose of silicate is used, the addition of magnesium did not result in any further improvements in brightness gain[28,31]. However, the addition of magnesium has been reported to result in an increased peroxide residual in the presence of an optimum level of silicate[30]. The stabilizing ability of magnesium during peroxide bleaching in the presence of silicate has been attributed to the formation of colloidal magnesium silicate which is believed to deactivate transition metal decomposition catalysts by adsorption[9,18].

1.4 Research Proposal

The use of hydrogen peroxide as an industrial bleaching agent for the brightening of mechanical pulps is becoming increasingly popular. Peroxide is capable of bleaching pulps to relatively high brightness levels without any of the adverse environmental effects which have been associated with chlorine and sulphur based bleaching chemicals. However, the efficiency of the bleaching process has been shown to be closely linked to the presence of transition metal ions, notably iron, copper and manganese, which can catalytically decompose peroxide leading to a loss in the active bleaching agent[18-31]. In order to achieve optimum bleaching responses it is therefore necessary to control these metal catalysed reactions[18-31]. Chelating agents are commonly use as a pretreatment to facilitate the removal of the metals[18,54,106], while stabilizing agent such as sodium silicate and magnesium salts are employed to reduce the harmful effects of remaining metals during bleaching[4,28,30,31].

The importance of controlling peroxide decomposition during bleaching has motivated a number of studies investigating the effects of stabilizers on the transition metal catalysed decomposition of alkaline hydrogen peroxide in the absence of pulp[24-27]. Unfortunately, the results of these studies have often been conflicting, with numerous different mechanisms proposed to account for the observed behaviour in the presence of various additives. An additional problem with studies of this type is that they fail to

consider the possible influences that the presence of pulp may exert on the peroxide decomposition behaviour. There have been relatively few studies of the effects of transition metals on peroxide decomposition in the presence of pulp, with the majority of these being of limited scope[19-22,96,146,147]. In contrast to the systems in the absence of pulp, there has been no systematic study of the effects of stabilizers on peroxide decomposition catalysed by individual transition metal ions in the presence of pulp.

The present investigation was conducted in an attempt to achieve three major objectives. The experimental results obtained for peroxide decomposition systems containing various metals and additives have, in the past, led to a wide range of mechanistic proposals. The first aim of the study was to determine if a general explanation exists for the phenomena observed during the metal catalysed decomposition of hydrogen peroxide in alkaline solutions. The second objective of the study was to investigate the effects of the inclusion of pulp on the peroxide decomposition behaviour. It is potentially of great importance to determine if the behaviour of transition metals and additives in the presence of pulp is truly reflected by studies which are carried out in the absence of pulp. The use of various model systems representing various individual components of the pulp provides simplified conditions in which to determine the reasons for any deviations in peroxide decomposition behaviour observed on the inclusion of pulp. The third component of this work involves the determination of the effects peroxide decomposition in the presence of various combinations of transition metals and additives on the bleaching response of a typical thermomechanical pulp.

CHAPTER 2

Mechanisms of Metal Catalysed Peroxide Decomposition and Stabilization by Additives

2.1 Introduction

The transition metal catalysed decomposition of hydrogen peroxide has been studied for many years[27,49,50,53,56], as under the brightening conditions used in the pulp and paper industry these reactions can lead to a loss of the active bleaching agent. It has been estimated that as much as 30% of the initial hydrogen peroxide charge may be decomposed in these undesirable side reactions[137]. The majority of studies have investigated the effects of iron, manganese and copper as these are present in relatively large quantities during bleaching of pulp, being introduced from both the wood itself and from contact with mill equipment and process liquors during pulping[18,20,22,127].

A wide range of chemicals have been tested as stabilizing agents for alkaline hydrogen peroxide systems[30]. Complexing agents such as EDTA and DTPA, which act by selectively binding to metal ions, are widely used in the pulp and paper industry[29,105]. Other reagents such as sodium silicate and magnesium salts are also commonly used to control peroxide decomposition[18,28,30]. However, the mechanisms by which these additives operate remain unclear despite a large number of attempts to resolve the issue[26-28,30,107,160-164]. In addition, the effect of these additives on peroxide decomposition in the presence of various transition metal ion catalysts is unpredictable, with stabilization observed for certain combinations, e.g. iron + magnesium[26,115], manganese + silicate[21,25,27], and accelerated rates of decomposition for other combinations, e.g. manganese + magnesium[26,27], copper + silicate[21,24,25]. The reasons for these variations in behaviour are not well understood.

The present work focuses on the catalytic decomposition of hydrogen peroxide in the presence of transition metal ions, with a particular emphasis on the effects of various additives. The investigation was aimed at finding a general explanation for the phenomena observed during peroxide decomposition. The transition metals examined

in this study were iron and copper, while the results of an analogous study into the effects of manganese[27] are also discussed. In addition to the common peroxide stabilizers magnesium and sodium silicate, the effects of zinc and aluminium, which have also been reported to stabilize peroxide during bleaching[20,146], have been investigated. The effects of sodium were examined for comparison, as sodium was expected to have little influence on the peroxide decomposition.

2.2 Peroxide Decomposition in the Absence of Added Metal Ions

Hydrogen peroxide decomposition in the absence of added transition metal ions has been reported to depend on a number of factors including the pH and temperature of the alkaline solution[24,27,48-50,52]. Figure 2.1 shows that at pH 10.8, for a given temperature in the range 20-50°C, the decomposition reaction was first-order with respect to total peroxide concentration. The pH of these solutions was not observed to vary significantly during the course of the reaction. This result is consistent with the findings of Abbot that for low levels of peroxide decomposition (<35%) there is little change in the pH[27]. Figure 2.2 shows that increasing the pH from 9.6 to 12.1 resulted in increased rates of peroxide decomposition at 20°C, with first-order kinetics observed at each pH level studied.

Under alkaline conditions, the decomposition of hydrogen peroxide has been attributed to an uncatalysed, homogeneous bimolecular reaction involving the perhydroxyl anion HO_2^- [45,51]. This "spontaneous" decomposition has been shown to be second-order with respect to peroxide concentration[47,52]. However, a number of studies have demonstrated that the alkali induced decomposition is retarded by the addition of chelating agents, suggesting that catalytic impurities play a major role in the decomposition reaction even under conditions of high purity[48-50,52]. Under the conditions used for typical peroxide bleaching liquors, the decomposition has been

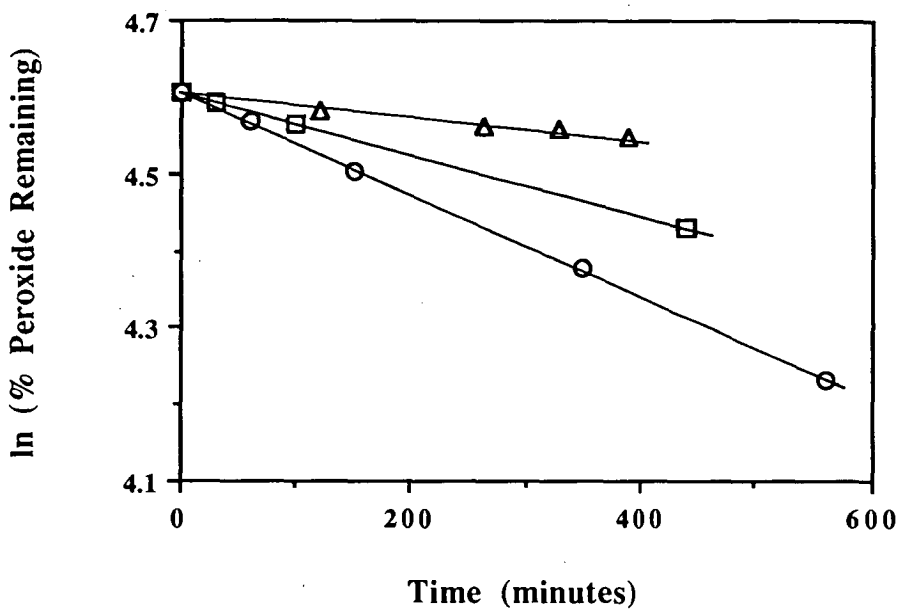

Figure 2.1 : First-order plots for decomposition of hydrogen peroxide in the absence of added metal ions at various temperatures. (Δ : 20°C ; □ : 35°C ; O : 50°C ; pH 10.8, initial $[H_2O_2] = 0.10M$).

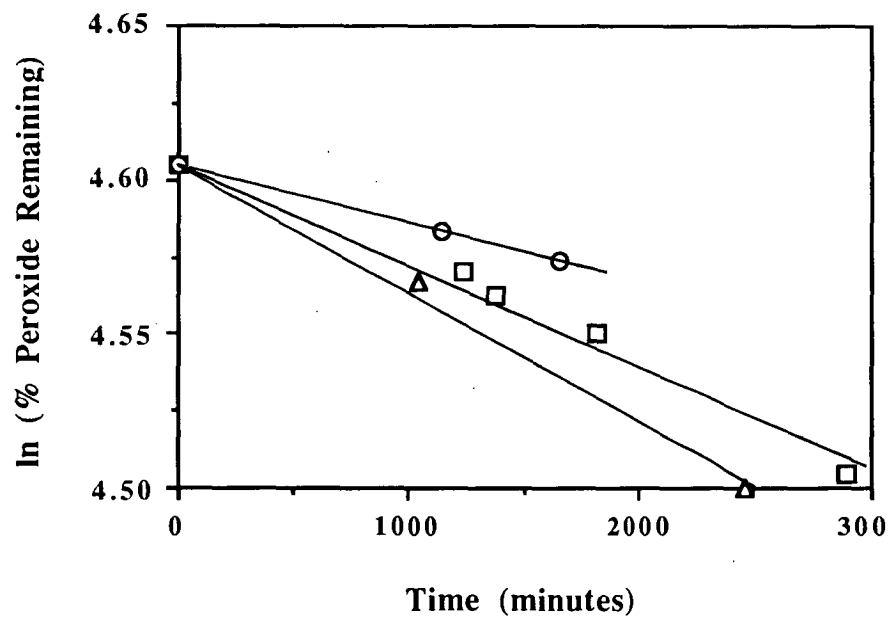

Figure 2.2 : First-order plots for decomposition of hydrogen peroxide in the absence of added metal ions at various pH levels. (O : pH 9.6 ; □ : pH 11.0 ; Δ : pH 12.1 ; 20°C, initial $[H_2O_2] = 0.10M$).

reported to be catalysed by transition metal impurities[53].

Many previous investigations on alkaline peroxide decomposition have noted the importance of purification of the alkali, as this is usually the source of metallic impurities[8,47,50]. Semiconductor grades of sodium and potassium hydroxide containing very low levels of trace metals are now commercially available and are well suited to this type of investigation (see section 7.1). The very low residual levels of metallic impurities appear to catalyse the first-order peroxide decomposition reactions in the absence of added metal ions.

Conditions chosen for the study of added transition metal ions were 20°C and a pH of ~11. The low temperature has the advantages of a relatively small "blank" reaction in the absence of added metal ions, and should also give relatively low rates of metal catalysed decomposition to facilitate the study of the kinetics of these reactions. The mechanisms of decomposition would not be expected to be significantly different from those observed under the higher temperatures typically found under industrial bleaching conditions. The rate constant for the "blank" reaction has been subtracted from the measured total rates of decomposition in the presence of added metal ions in all subsequent experiments to obtain the value for the rate of metal catalysed decomposition[57].

2.3 Iron-Catalysed Decomposition of Hydrogen Peroxide

Results for peroxide decomposition at 20°C in the presence of iron at pH 11.0 are shown in Figure 2.3. There is clearly a non-linear relationship between time and the logarithm of peroxide concentration, unless only the initial reaction period is considered. This indicates that, under alkaline conditions, decomposition in the presence of iron cannot simply be represented by a first-order kinetic expression with

respect to hydrogen peroxide concentration, as has been reported[168,169]. Other studies have also recognised that this system is indeed more complex than can be represented by a simple first-order process[49,50]. One analysis of kinetic data was interpreted on the basis of two parallel decomposition pathways[50]. The first route was reported to depend on the concentration of undissociated hydrogen peroxide and the alkalinity of the solution for a given metal ion concentration, while the second was independent of the concentration of molecular hydrogen peroxide[50].

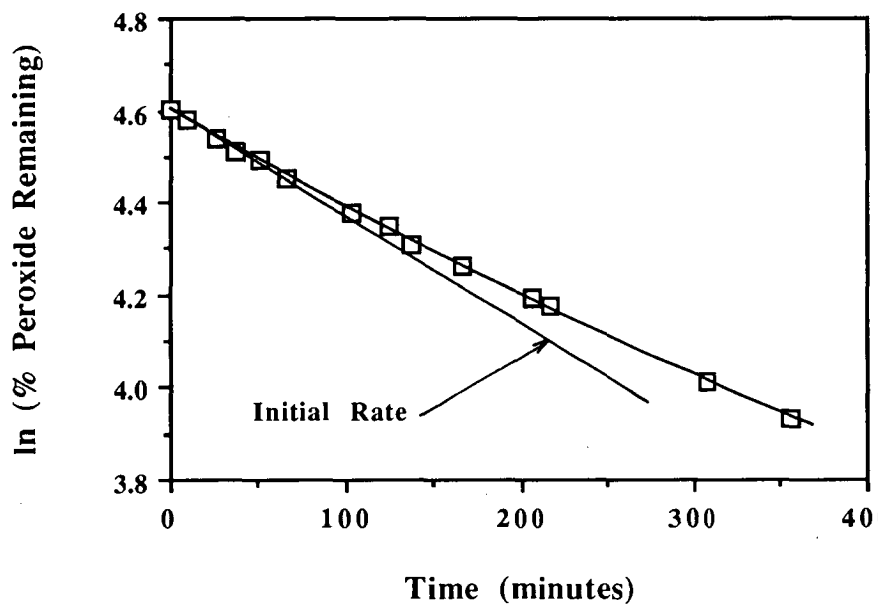

Figure 2.3 : Logarithmic plot for decomposition of hydrogen peroxide in the presence of added iron. (20°C, pH 11.0, [Fe] = 1.98×10^{-4} M, initial $[H_2O_2] = 0.10$M).

An alternative, and probably more fruitful approach, is to recognize that the catalytic species itself evolves with time, and this will be reflected in any kinetic analysis which examines the relationship between decomposition rate and peroxide concentration, as time progresses. A declining concentration of the active catalytic species may also

explain why apparent orders of reaction in the range 1.8-2.0 with respect to peroxide have been reported[49].

It is well known that aqueous solutions of Fe^{3+} undergo hydrolysis to give complex mixtures of species[170-172], dependent on both pH and time. Hydrolysis products range from simple monomeric species such as $FeOH^{2+}$, through dimers and trimers, including $Fe_2(OH)_2^{4+}$, to polymeric species represented by $[Fe(OH)_x(NO_3)_{3-x}]_n$ where n~900[173]. The behaviour of such systems has been studied in detail at low pH[174-178], where attainment of equilibrium can occur very slowly, even requiring weeks or months. The evolution of iron species in strongly alkaline media appears to be less well defined, although it is established that solutions "age" with time, and the aged iron species are less active towards decomposition of hydrogen peroxide[25,179]. Aging of these iron solutions appears to be accompanied not only by an increased degree of polymerization, but also by replacement of hydroxy bridges by oxy bridges in the polynuclear iron species[180,181].

Figure 2.4 shows the variation in initial first-order rate constant for iron catalysed peroxide decomposition at pH 11.0 as the solution was allowed to age prior to the addition of hydrogen peroxide. Aging of these solutions took place at pH 12.1, and the addition of hydrogen peroxide was accompanied by a reduction in the pH of the solution. It is apparent that aging of the solution was accompanied by an initial rapid decline in catalytic activity of the species present. After about 20 hours a constant level of activity was reached. The limiting value of the rate constant was observed to be almost independent of pH, as shown in Figure 2.5. However, this figure also shows that the first-order rate constant for initial decomposition of hydrogen peroxide does depend on the pH of the solution and exhibits a maximum at pH ~11. A maximum in decomposition at pH ~11 in the presence of iron has been reported previously[49].

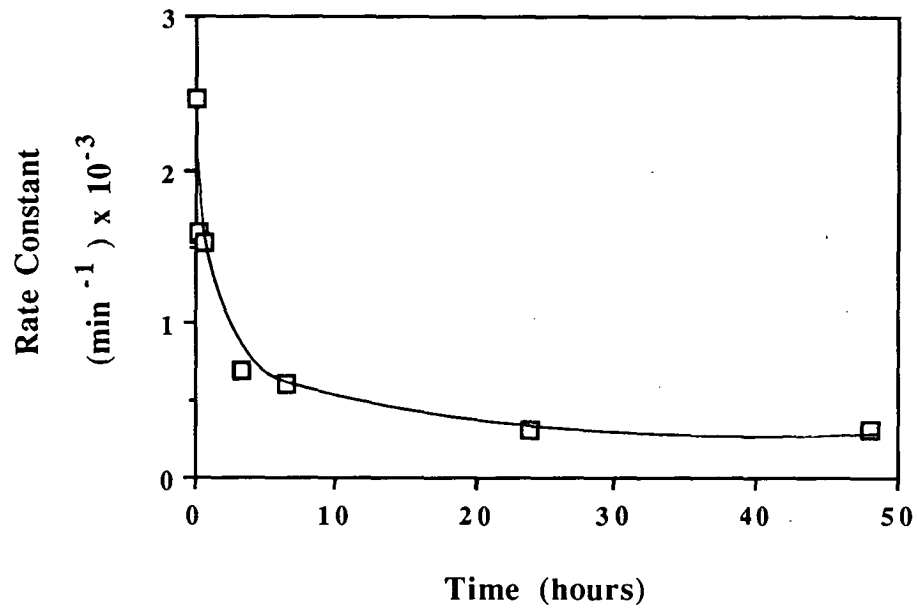

Figure 2.4 : Effect of aging of added iron on initial reaction rates for the decomposition of hydrogen peroxide. (20°C, pH 11.0, [Fe] = 1.98×10^{-4} M, initial $[H_2O_2] = 0.10M$)

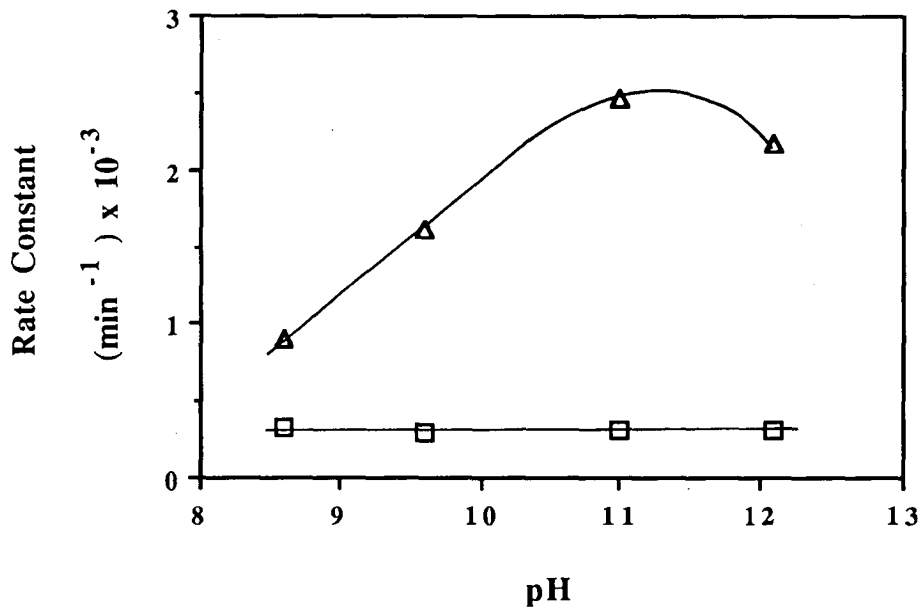

Figure 2.5 : Effect of pH on initial reaction rate (Δ) and for systems aged 48 hrs (□) for iron catalysed decomposition of hydrogen peroxide. (20°C, [Fe] = 1.98×10^{-4} M, initial $[H_2O_2] = 0.10M$).

2.3.1 Effects of Magnesium

A brown colouration was observed for alkaline ferric nitrate solutions in the absence of magnesium. A previous study has attributed the brown colouration to an optically empty sol of ferric hydroxide which forms on the auto-hydrolysis of dilute solutions of ferric iron[182]. Addition of magnesium nitrate to freshly prepared alkaline solutions of ferric nitrate at 20°C resulted in precipitation within a few minutes. For systems with pH above 9 and concentrations of magnesium in excess of ~$1.2x10^{-3}$ M, the precipitate dissolved to produce a clear colourless solution. For additions of magnesium nitrate of less than ~$1.2x10^{-3}$ M, the precipitate did not completely dissolve. Dispersion of these precipitates by rapid stirring produced solutions containing a brown coloured colloidal suspension, with the intensity of the brown colouration decreasing as the concentration of magnesium was increased.

The formation of the brown colouration in solutions containing various levels of iron has been quantified using UV-visible spectroscopy by Ant-Wuorinen and Visapaa[182]. While no distinct absorbance maximum was observed, the aging of the iron solution could be followed by measuring the absorbance at an arbitrarily chosen wavelength[182]. Gilbert et al. also used absorption measurements to follow the interaction of iron with magnesium in the presence of gluconic acid, using a 40% ethanol solution to enhance the ferric absorption bands[115].

Figure 2.6 shows absorbance spectra in the UV-visible region for several solutions containing iron and magnesium at pH 12.1. This shows there was a significant change in absorbance as magnesium was introduced, which suggests there must also be a change in the nature of the chemical species present. Figure 2.7 shows the variation in absorbance of these solutions at an arbitrary wavelength in the visible region (376nm), with increasing magnesium concentration. A marked discontinuity in absorbance was

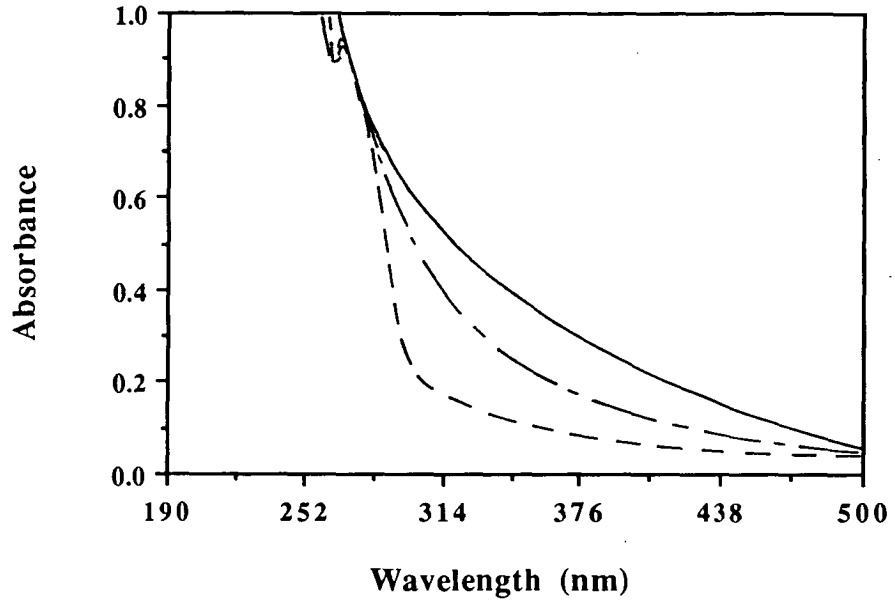

Figure 2.6 : UV-visible absorbance spectra for solutions containing added iron in the presence of magnesium. (———: [Mg] = 0 ;—— -: [Mg] = 5.94×10^{-4} M ;– – – : [Mg] = 1.19×10^{-3} M ; 20°C, pH 12.1, [Fe] = 1.98×10^{-4} M, no H_2O_2 present).

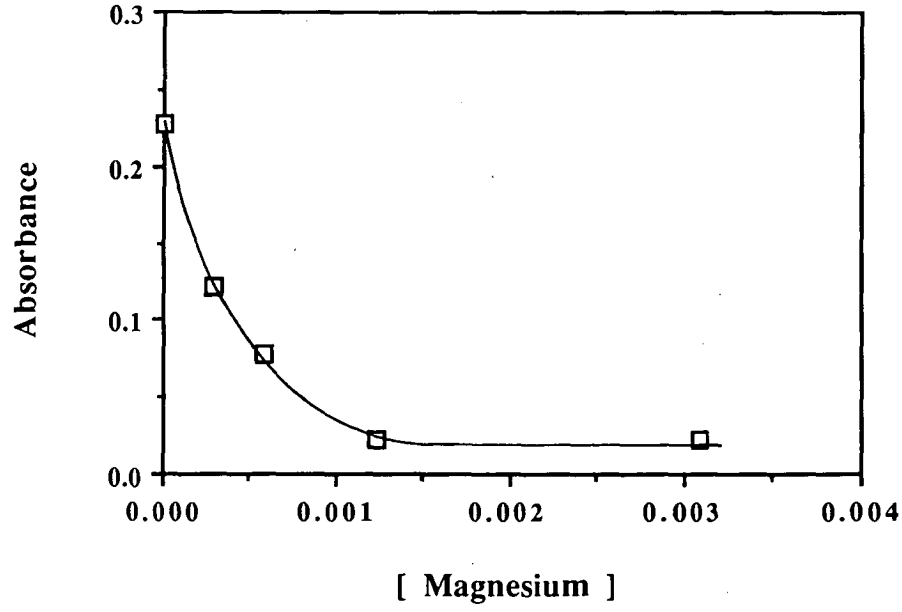

Figure 2.7 : Variation in absorbance at 376nm of solutions containing iron with increasing magnesium dose. (20°C, pH 12.1, [Fe]=1.98×10^{-4}M, no H_2O_2 present).

observed at a concentration of magnesium of ~$1.2x10^{-3}$ M, which corresponds to a magnesium to iron molar ratio of ~6:1. A discontinuity in visible absorbance spectra corresponding to a molar ratio of 6:1 for Mg:Fe in similar solutions containing gluconic acid has previously been reported[115].

Peroxide decomposition experiments were carried out at pH 11.0 for various levels of magnesium addition. Solutions containing the desired amounts of ferric nitrate and magnesium nitrate were prepared at pH 12.1 and aged for one hour. A drop in pH to 11.0 was observed upon addition of hydrogen peroxide. Figure 2.8 shows the initial decomposition in the presence of magnesium can be represented by first-order kinetics. Figure 2.9 shows how the first-order rate constants varied with increasing magnesium concentration. It is apparent that increasing the magnesium addition produced a reduction in the initial rate of peroxide decomposition, particularly for a concentration of ~$1.2x10^{-3}$ M or greater. Comparing Figures 2.7 and 2.9, a general correlation between the absorbance of the species present and the magnitude of the initial first-order rate constant for peroxide decomposition can be seen.

It is well established that many metal ions undergo hydrolysis in aqueous solution[181,183,184]. For metal ions M^{n+}, where $n \geq 2$, hydrolysis usually leads to complex species containing more than one metal centre, linked through oxy or hydroxy bridges[181,183,184]. The hydrolysis of iron in particular has been studied in detail[172-178], with structural units of the type Fe-O-Fe combining to produce polymeric complexes. Magnesium ions are also known to undergo hydrolysis in aqueous solution[184-186], with the formation of polynuclear complexes of the type $Mg_2(OH)_2^{2+}$ and $Mg_3(OH)_4^{2+}$ [185,186]. These considerations lead to the possibility of mixed binuclear hydrolysis complexes when both iron and magnesium are present in the aqueous alkaline medium, giving rise to linkages of the type Fe-O-Mg. Formation of this type of structural unit, where the redox centres (ie iron atoms) are separated by the

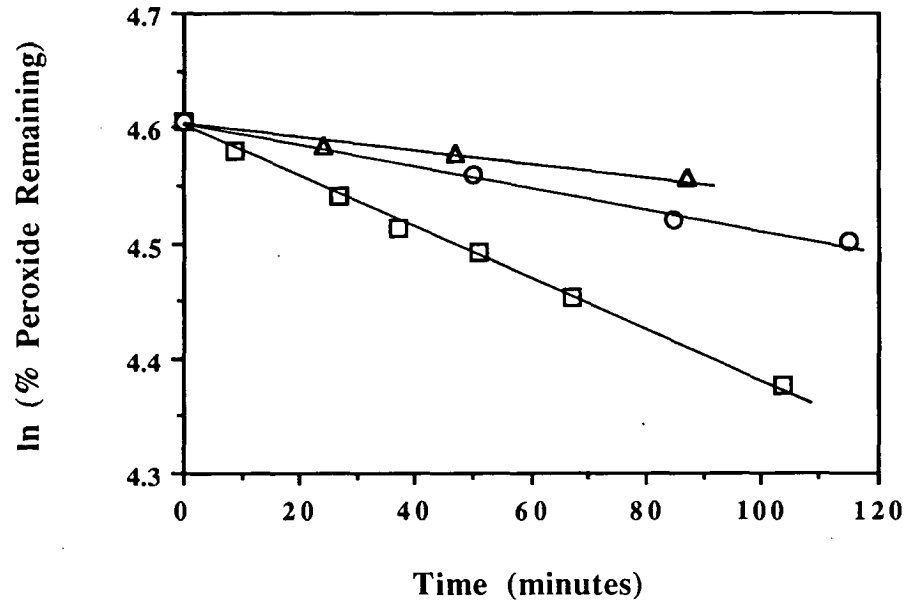

Figure 2.8 : First-order plots for peroxide decomposition in the presence of iron and various levels of magnesium. (□ : [Mg] = 0 ; ○ : [Mg] = 5.94×10^{-4} M ; △ : [Mg] = 2.97×10^{-3} M ; 20°C, pH 11.0, [Fe] = 1.98×10^{-4} M, initial $[H_2O_2]$ = 0.10M).

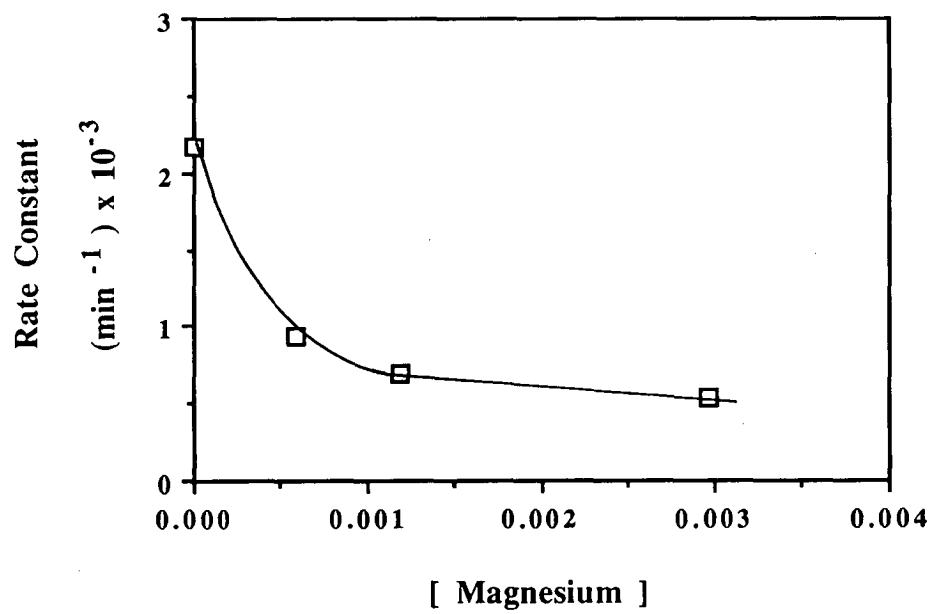

Figure 2.9 : Variation in initial first-order rate constants for peroxide decomposition in the presence of iron and various levels of magnesium. (20°C, pH 11.0, [Fe]=1.98×10^{-4} M, initial $[H_2O_2]$ = 0.10M).

insertion of Mg atoms, could be expected to influence properties of the resulting species, including absorbance and catalytic activity.

The concept of complex formation between iron and magnesium has been discussed previously in conjunction with stabilization of hydrogen peroxide solutions[85,114,115]. Sinkey and Thompson concluded from a polarographic study that magnesium stabilizes alkaline hydrogen peroxide by interacting directly with ferric ions[114]. However, the nature of the interaction was not determined[114]. Gilbert et al. proposed the formation of soluble magnesium-iron complexes with molar ratios of 3:1 and 6:1 in the presence of gluconic acid, with bonding between the iron and magnesium via hydroxo (-OH-) or oxo (-O-) bridges[115]. The role of the gluconic acid in the formation of the complexes was not clear, but it was thought to play an important role in maintaining the homogeneity of the system[115]. Isbell et al. also attributed the inhibition of the catalytic effect of iron in the presence of D-glucose to the formation of a magnesium-iron complex containing 6 moles of magnesium to 1 mole of iron[85]. These workers proposed that the structure of the complex was analogous to that of a ferrocyanide or ferricyanide[85]. In the absence of gluconic acid the stabilization has been attributed to adsorption onto, or coprecipitation with insoluble magnesium hydroxide[46,47].

2.3.3.1 Aging Phenomena and the Iron-Magnesium Complex

Addition of magnesium to freshly prepared alkaline iron solutions with pH > 9 and a magnesium concentration greater than ~1.2×10^{-3} M was observed to give clear colourless solutions after dissolution of the initially formed precipitates. In contrast, addition of magnesium to iron solutions aged for 24 hours at similar pH levels produced no significant change in the absorbance spectra in the visible range. It can be concluded that magnesium interacts only with initially produced hydrolysis products

from Fe^{3+} to form the colourless complex. Although magnesium may also interact with the aged species, as indicated by the reported stabilization of aged iron by magnesium[26], the products formed do not give rise to observable changes in the visible absorbance spectra. This property can be used to follow the progress of the aging process.

Iron solutions at pH 12.1 were allowed to age for various periods, after which magnesium nitrate was added to give a concentration of ~3.0×10^{-3} M, to provide a large excess of magnesium. The resulting mixtures were allowed to stand for at least an hour, then vigorously stirred, and the absorbance spectrum measured in the visible region. The resulting series of spectra were intermediate between those obtained for the freshly prepared and the fully aged (24 hours) samples. Figure 2.10 shows the difference in the measured absorbance at 376nm between freshly prepared and aged iron after addition of magnesium as the duration of aging was increased. This shows that the absorbance at this wavelength decreases rapidly during the initial aging period, after addition of magnesium, reaching a constant value after an aging period of ~10 hours, following the general behaviour of the activity profile shown in Figure 2.4.

The correlation between the activity of the iron species present at various times and the formation of the iron-magnesium complex, as reflected by the absorbance measurements can be considered further. Figure 2.11 shows the change in initial activity of the iron species present, plotted as a percentage (θ) of initial activity, as aging progresses. These values can be compared with those for θ_{Abs}, calculated according to the expression

$$\theta_{Abs} = \left[\frac{k_F(A_A - A_S)}{(A_A - A_F)} + \frac{k_A(A_S - A_F)}{(A_A - A_F)} \right] \times 100\%$$

where k_F and k_A are the first-order rate constants for peroxide decomposition catalysed

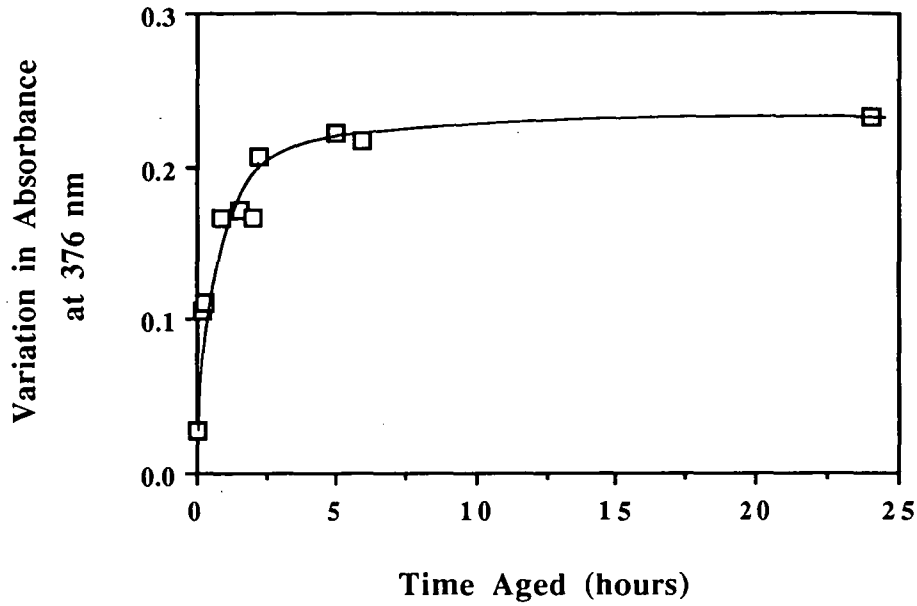

Figure 2.10 : Variation in absorbance at 376nm with aging of iron in alkaline solutions, followed by the addition of magnesium. ([Mg] = 2.97×10^{-3} M, 20°C, pH 12.1, [Fe] = 1.98×10^{-4} M, no $[H_2O_2]$ present).

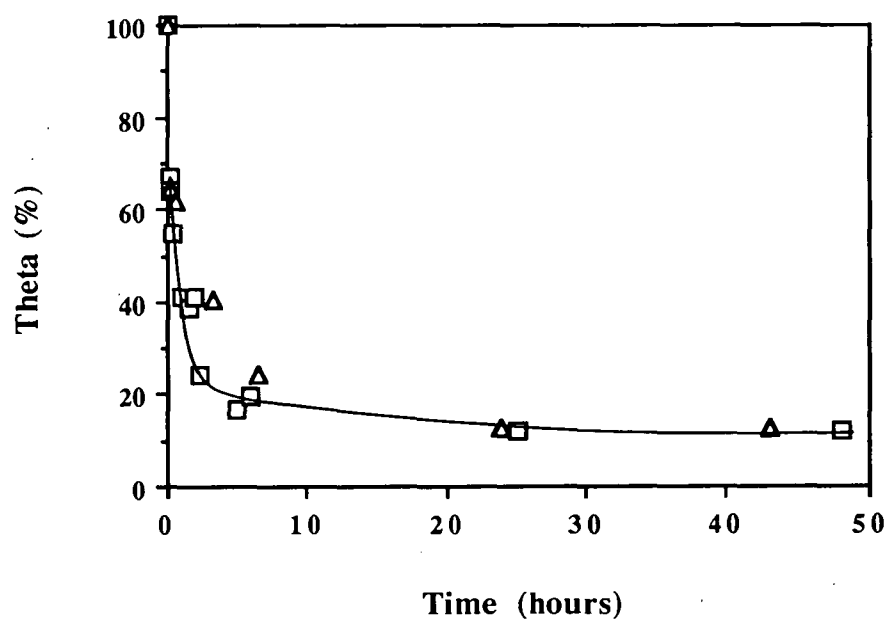

Figure 2.11 : Correlation between observed initial rate of peroxide decomposition (△) and rates calculated from absorbance measurements (□).

by the fresh and fully aged iron respectively; A_F, A_A and A_S are the absorption values for fresh, fully aged and partially aged samples respectively.

This expression assumes that the iron is either present as the more active initially formed species which complexes with magnesium, or a second less active species, and that the former is converted directly to the latter. This will almost certainly represent a simplification, as there are likely to be more than two hydrolysis products present at any particular time[171,172]. However, Figure 2.11 demonstrates that there is a reasonable correlation between θ and θ_{Abs}. This indicates that there is a direct relationship between peroxide decomposition rate and the presence of highly active initial hydrolysis products of Fe^{3+} which can react with magnesium to produce the colourless complex.

2.3.2 Effects of Sodium Silicate and Aluminium

The initial iron catalysed decomposition of hydrogen peroxide at pH 11.0 in the presence of various levels of sodium silicate and aluminium can also be represented by first-order kinetics, in the same way as magnesium. Solutions were prepared by addition of ferric nitrate to alkaline (pH 12.1) solutions containing the desired amount of sodium silicate or aluminium nitrate, with the subsequent addition of hydrogen peroxide lowering the pH to 11.0.

Figure 2.12 shows how the observed first-order rate constants varied with increasing silicate concentration. It is apparent that a reduction in the initial rate of peroxide decomposition was achieved by the introduction of increasing amounts of silicate, particularly up to a concentration of ~2.0×10^{-2} M. As for addition of magnesium, addition of silicate under alkaline conditions in the presence of iron produced a change in the complex species present. This was reflected by the decreasing absorbance of the

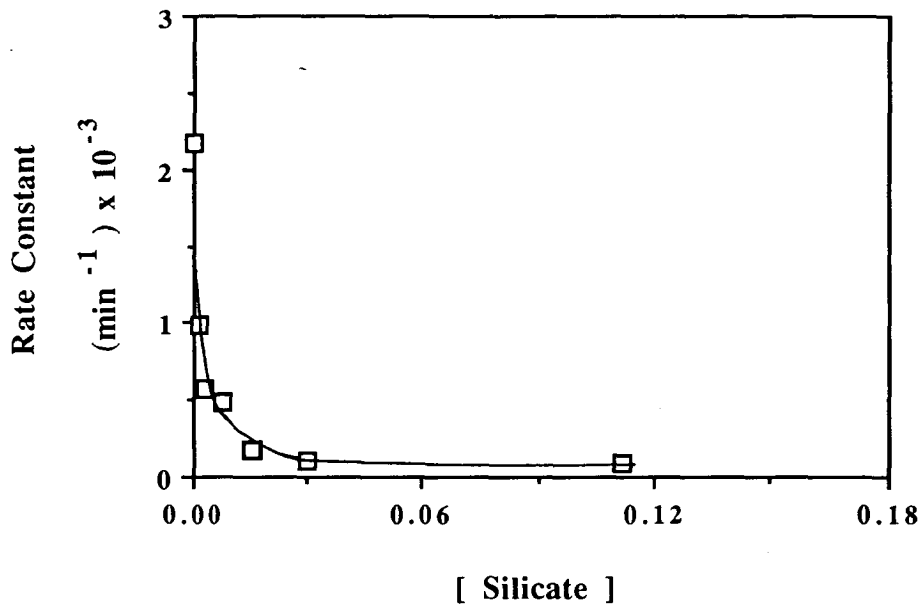

Figure 2.12 : Variation in initial first-order rate constants for peroxide decomposition in the presence of iron and various levels of sodium silicate. (20°C, pH 11.0, [Fe] = 1.98×10^{-4} M, initial $[H_2O_2]$ = 0.10M).

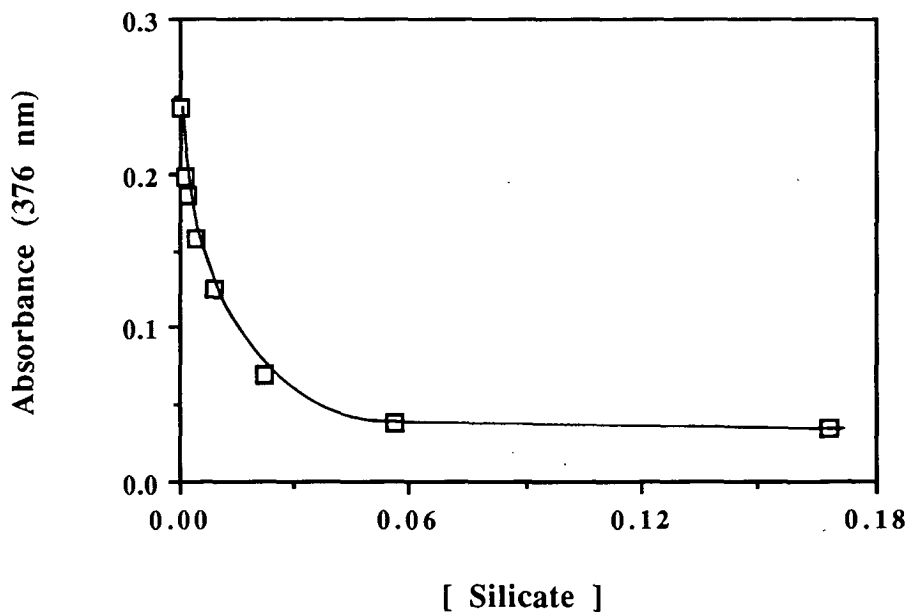

Figure 2.13 : Variation in absorbance at 376nm of solutions containing iron as the silicate level is increased. (20°C, pH 12.1, [Fe] = 1.98×10^{-4} M, no $[H_2O_2]$ present).

solutions as shown in Figure 2.13. Comparison of Figures 2.12 and 2.13 shows both the decrease in first-order rate constant and development of the Fe-Si complex species occurred over the same range of silicate addition. The minimum value for the rate constant, indicating maximum stabilization of the peroxide system, was observed for a silicate concentration of ~2.0×10^{-2} M, which also corresponds to the minimum value for the absorbance of the species present.

Variation in the initial first-order rate constant for peroxide decomposition at pH 11.0 corresponding to addition of aluminium to the alkaline iron system is shown in Figure 2.14. In this case the minimum value for the initial rate constant was achieved upon raising the aluminium concentration to ~1.0×10^{-2} M, which also corresponds to the concentration for the minimum absorbance of the species present to be reached (Figure 2.15).

Both aluminium[187-191] and silicate[192-198] are known to undergo hydrolysis in aqueous solutions. Aluminium is reported to form polynuclear complexes of the type $Al_2(OH)_2^{4+}$ and $Al_3(OH)_4^{5+}$ [189,190]. The extent of aluminium hydrolysis has been reported to depend on the OH:Al ratio under conditions used in papermaking applications, where alum plays a number of important roles[191]. Polynuclear species which have been reported for silicate under alkaline conditions include $Si_2O_3(OH)_4^{2-}$ and $Si_4O_6(OH)_6^{2-}$ [192,193]. The formation of colloidal polysilicic acid species in solutions of sodium silicate has also been discussed[195-197]. Monomeric silicic acid can polymerise to form colloidal polysilicic particles, which can then add more monomeric silicic acid by condensation on the surface[197]. The polymeric particles can aggregate by physical bonding and crosslinking reactions and finally the colloidal sol is transformed into a gel[197]. The formation of colloidal silicate species is reported to occur in alkaline solutions above pH 10.6 and also in concentrated solutions of silicic acid[195]. The copolymerisation of metals with silicic acid has also been investigated,

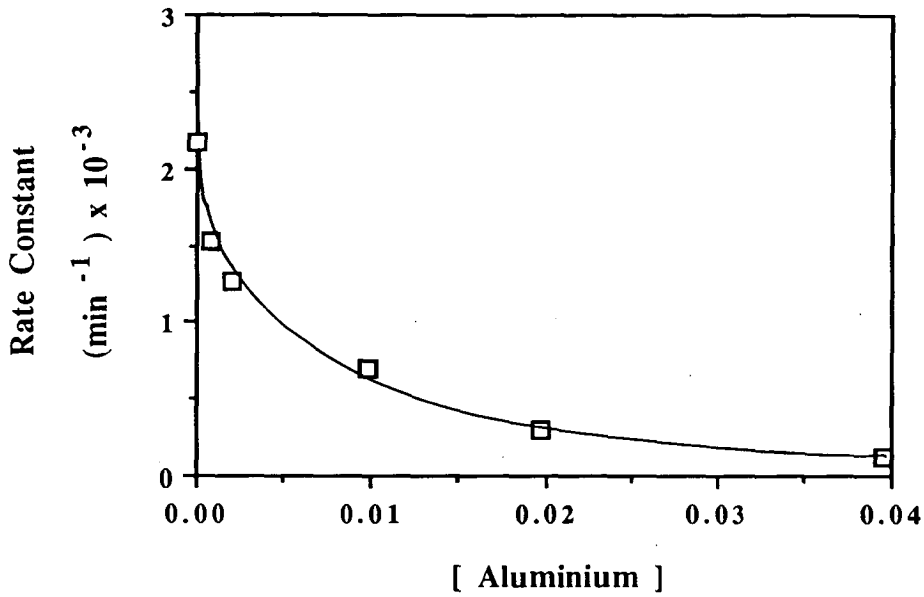

Figure 2.14 : Variation in initial first-order rate constants for peroxide decomposition in the presence of iron and various levels of aluminium. (20°C, pH 11.0, [Fe] = 1.98×10^{-4} M, initial $[H_2O_2] = 0.10$M).

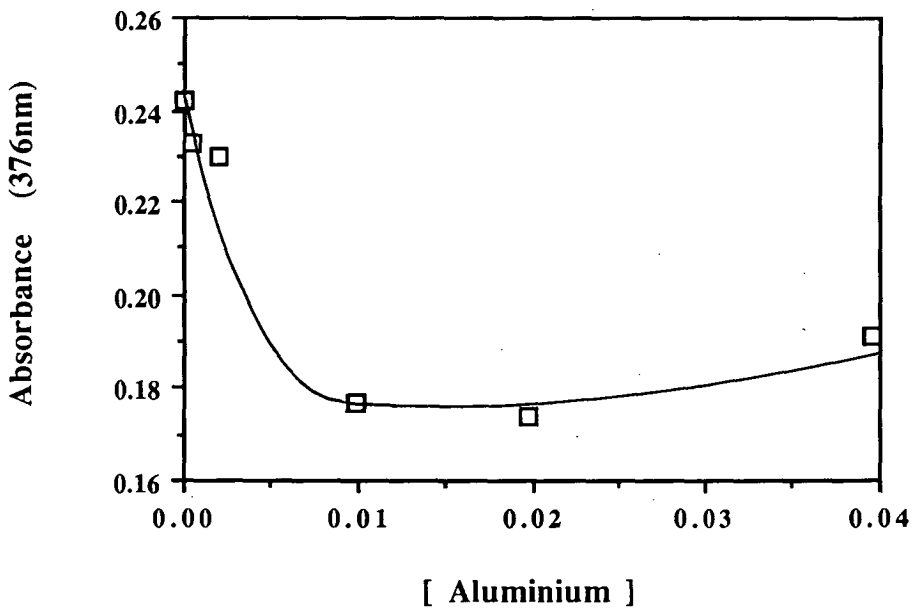

Figure 2.15 : Variation in absorbance at 376nm of solutions containing iron as the aluminium level is increased. (20°C, pH 12.1, [Fe]=1.98×10^{-4}M, no $[H_2O_2]$ present).

with the formation of bonds of the type Si-O-M established from Infra Red spectra of the precipitates[199].

As in the case of magnesium, it seems reasonable to assume that mixed polynuclear species can be formed between iron and either aluminium or silicate under alkaline conditions. Such species would contain structural units of the type Fe-O-Al or Fe-O-Si, replacing the dimeric Fe-O-Fe units formed by hydrolysis of Fe^{3+} in the absence of aluminium and silicate.

2.3.3 Effects of Sodium and Zinc

Metal ions with a single positive charge (Na^+,K^+) show much less tendency to undergo hydrolysis to form dimeric and polymeric bridged species in aqueous solution. Figure 2.16 shows addition of sodium to an alkaline (pH 11.0) hydrogen peroxide solution containing iron had virtually no effect on the initial first-order rate constants for peroxide decomposition. Similarly, very little change in absorbance was observed as the sodium concentration was increased (Figure 2.17). The lack of influence on the catalytic properties of the iron species present is not unexpected, as strong coupling of Fe-O-Na centres was not anticipated.

The Zn^{2+} ion is known to undergo hydrolysis in aqueous solution, with formation of polynuclear species such as $Zn_2(OH)^{3+}$ and $Zn_3(OH)_3{}^{3+}$ reported for alkaline conditions[200-203]. However, unlike the behaviour observed in the presence of magnesium, silicate or aluminium, the addition of zinc to the alkaline system containing iron was observed to result in increased initial first-order rate constants for peroxide decomposition (Figure 2.18). Difficulties were experienced in measuring absorbance spectra of the solutions due to the presence of a thick, white colloidal suspension which formed immediately upon addition of zinc. It seems plausible that

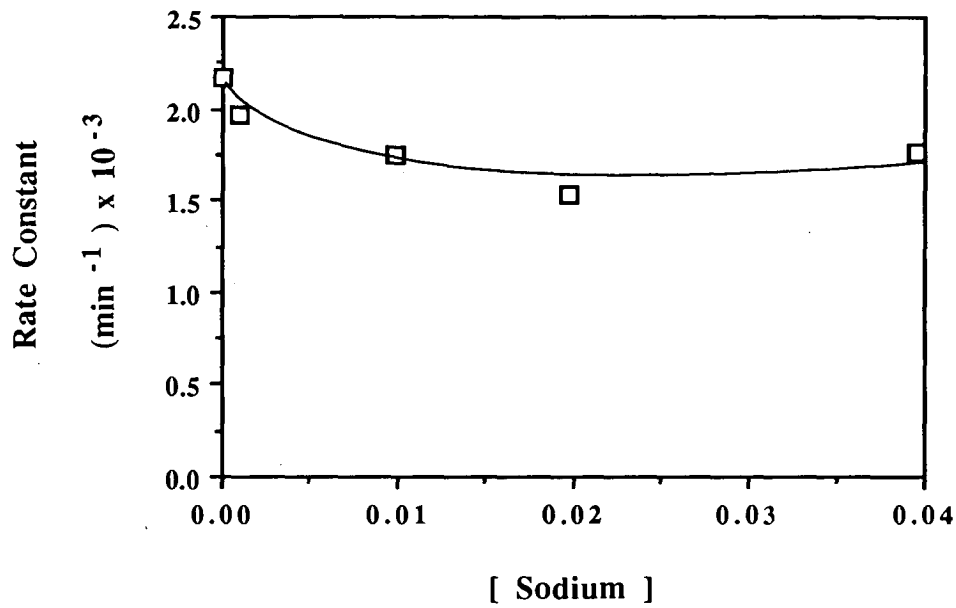

Figure 2.16 : Variation in initial first-order rate constants for peroxide decomposition in the presence of iron and various levels of sodium. (20°C, pH 11.0, [Fe] = 1.98×10^{-4} M, initial $[H_2O_2]$ = 0.10M).

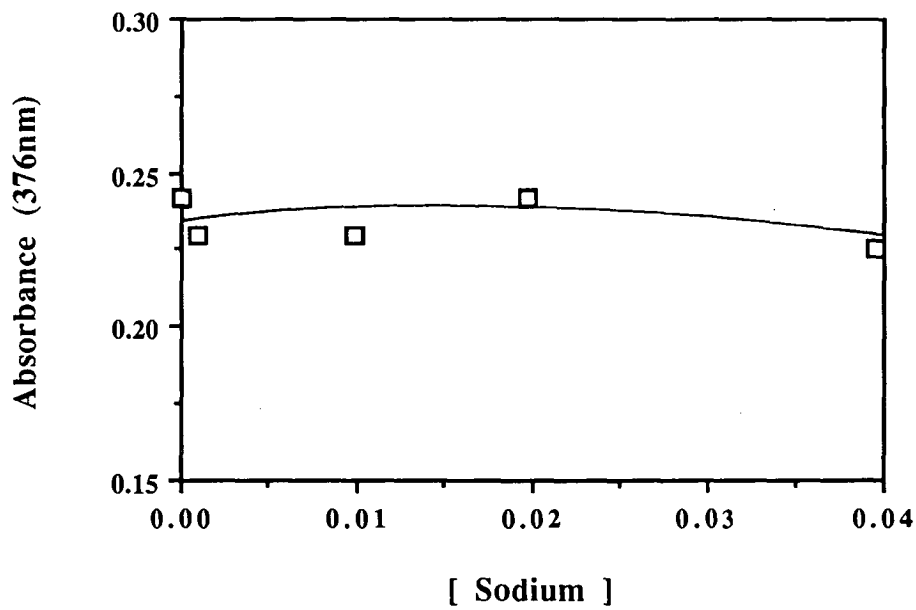

Figure 2.17 : Variation in absorbance at 376nm of solutions containing iron as the sodium level is increased. (20°C, pH 12.1, [Fe] = 1.98×10^{-4} M, no $[H_2O_2]$ present).

the formation of a mixed hydrolysis species between zinc and iron may occur, with the resultant species having increased catalytic activity.

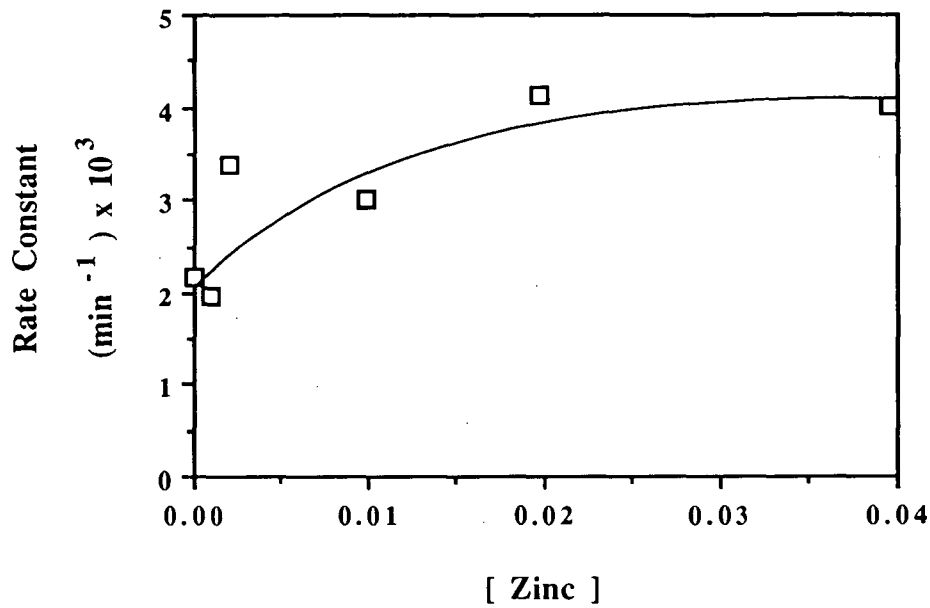

Figure 2.18 : Variation in initial first-order rate constants for peroxide decomposition in the presence of iron and various levels of zinc. (20°C, pH 11.0, [Fe]=1.98x10^{-4} M, initial [H_2O_2] = 0.10M).

2.3.4 Summary of Decomposition in Presence of Iron

This study has shown that there are correlations between catalytic activity towards decomposition of alkaline hydrogen peroxide and the presence of complex species formed through interaction of iron and other elements such as magnesium, silicate, zinc and aluminium. The presence of such species can be followed by physical techniques such as absorbance of the solution, prior to addition of hydrogen peroxide. This measurement can in turn be related to a kinetic measurement, the initial first-order rate constant for peroxide decomposition. An order of reactivity towards the formation

of mixed polynuclear species of the type Fe-O-M (where M = Mg, Al, Si) can be derived from the results of both absorbance measurement and rate determination experiments. Comparing the concentrations of additives required for maximum effect, it is clear that magnesium has a higher affinity towards the formation of complexes of this type than aluminium, which in turn is more reactive than silicate.

The behaviour in the presence of zinc was found to be different from that observed for the other additives, in that the catalytic activity of the iron was enhanced and not reduced. It seems likely that a species formed through the direct interaction of the zinc and iron is responsible for the increased catalytic activity. In the presence of sodium, where no interaction with iron was observed, there was little change in the catalytic activity.

The iron catalysed decomposition behaviour in the absence of additives has been shown to be closely related to the aging of the iron species present. The rapid peroxide decomposition rates observed for freshly prepared solutions of Fe^{3+} can be attributed to the presence of initial hydrolysis species, while the species present following further aging are less active towards peroxide decomposition. The formation of a complex between magnesium and the initial hydrolysis species of iron results in a colourless solution, while iron species formed on aging do not undergo the reaction to give the colourless complex. This allows the aging process to be studied directly, and a good correlation is observed between the relative concentrations of the iron species present and the rate of decomposition.

2.4 Copper Catalysed Decomposition of Hydrogen Peroxide

Results for peroxide decomposition at pH 11 in the presence of copper, which had been aged at pH 12.0 for various times are shown in Figure 2.19. The reaction can

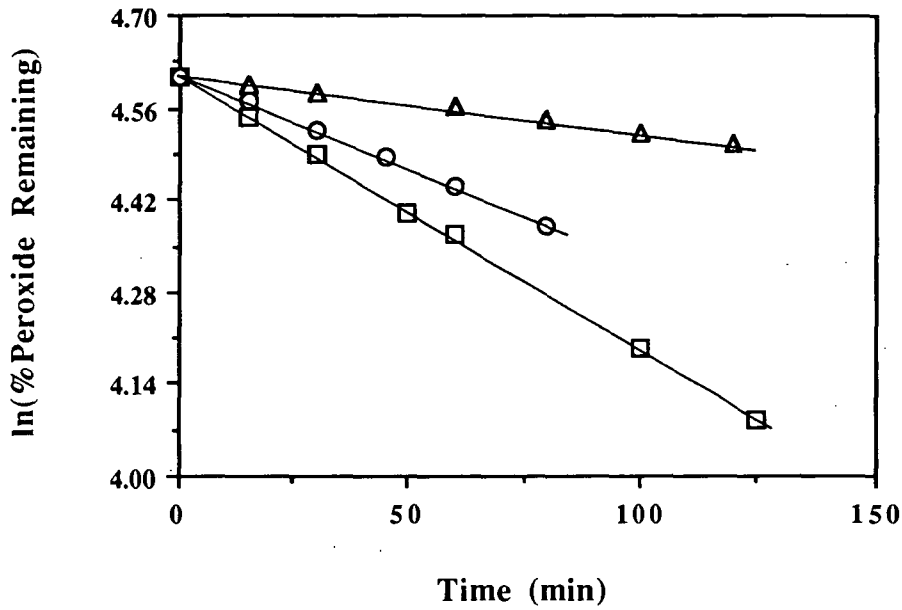

Figure 2.19 : First-order plots of peroxide decomposition with aged copper catalysts. (□ : fresh Cu ; ○ : Cu aged 240 min ; △ : Cu aged 1200 min ; 20°C, pH 11.0, [Cu] = 2.14×10^{-4} M, initial $[H_2O_2] = 0.10$ M).

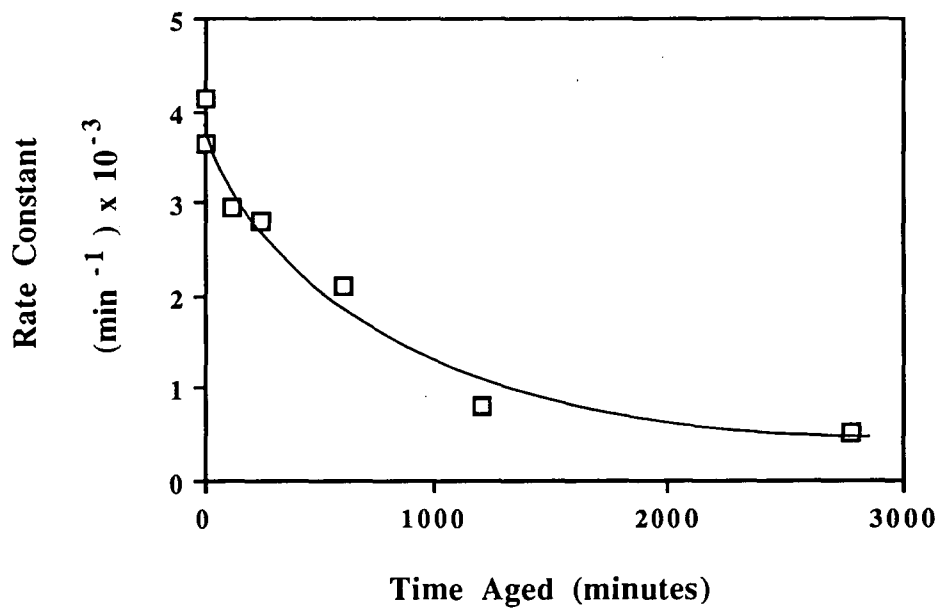

Figure 2.20 : Variation in first-order rate constants for peroxide decomposition as copper is aged. (20°C, pH 11.0, [Cu] = 2.14×10^{-4} M, initial $[H_2O_2] = 0.10$ M).

clearly be represented by first-order kinetics with respect to total peroxide concentration over the period studied, with the rate decreasing as the copper was aged. The activity reached a constant level on aging the copper for ~1000 minutes, with little change observed on aging for a further 1500 min, as shown in Figure 2.20. Similar behaviour was observed for the decomposition of hydrogen peroxide in the presence of iron (section 2.3), which can be explained by the iron undergoing hydrolysis and polymerisation reactions to produce species which have differing catalytic activities. The hydrolysis of copper in aqueous solutions is well established[204,205], with species such as $[Cu(OH)]^{+}$, $[Cu_2(OH)_2]^{2+}$ and $[Cu_3(OH)_4]^{2+}$ containing linkages of the type Cu-O-Cu[204]. The behaviour of such systems has been studied in detail at low pH[204] and, although less well defined in strongly alkaline solutions, it can be assumed that the catalytically active copper species evolves with time.

Examination of the initially clear copper solutions, prior to peroxide addition, revealed the formation of a dark brown precipitate after ~600 minutes, with increasing quantities observed on further aging in the form of small aggregated particles. Addition of peroxide to solutions containing fresh copper results in the immediate formation of a brown colouration. This behaviour is well established[68] and has been attributed to the formation of a copper-peroxide complex[68,88]. While the exact structure of the copper-peroxide complex has been the subject of considerable discussion in the literature[69], its importance as an intermediate in the decomposition reaction has been established[69]. The addition of EDTA was reported to suppress the formation of the coloured complex resulting in a suppression of the rate of decomposition[69].

2.4.1 Effects of Magnesium

The introduction of magnesium to the system containing fresh copper and hydrogen peroxide resulted in a significant decrease in the rate of peroxide decomposition. Figure 2.21 shows the variation in first-order rate constant as the magnesium concentration was increased. Maximum stabilization was achieved for a magnesium concentration of ~1.3×10^{-3} M, with further magnesium additions giving little change. A similar optimum magnesium concentration was observed previously for the Fe/Mg system (section 2.3.1). The addition of magnesium also had the effect of reducing the colour formation due to the copper-peroxide complex. For magnesium concentrations of > ~1.3×10^{-3} M the solutions were essentially colourless, whereas a dark brown solution was observed in the absence of magnesium. This indicates that the magnesium must interact with the copper, resulting in a change in the chemical species present, where the resultant copper-magnesium species does not interact with peroxide to give a coloured complex. Figure 2.22 shows the change in absorbance at an arbitrary wavelength in the visible region (440nm) as the magnesium concentration was increased, and shows that a correlation exists between the catalytic activity towards peroxide decomposition and the formation of a new chemical species resulting from an interaction between magnesium and copper.

As observed with iron, the possibility arises of mixed binuclear hydrolysis complexes containing linkages of the type Cu-O-Mg. Formation of this type of structural unit, where the redox centres (ie copper atoms) are separated by insertion of magnesium, could be expected to influence the catalytic activity of the resulting species and could also affect its ability to form complexes with peroxide species, thus changing the absorbance characteristics of the solutions.

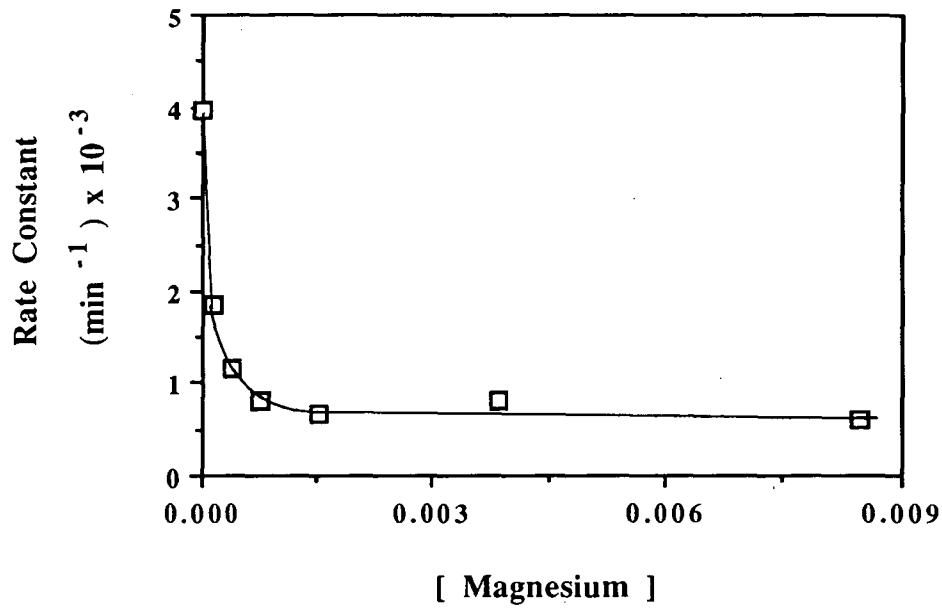

Figure 2.21 : Variation in initial first-order rate constants for peroxide decomposition in the presence of copper and various levels of magnesium. (20°C, pH 11.0, [Cu] = 2.14×10^{-4} M, initial $[H_2O_2]$ = 0.10M).

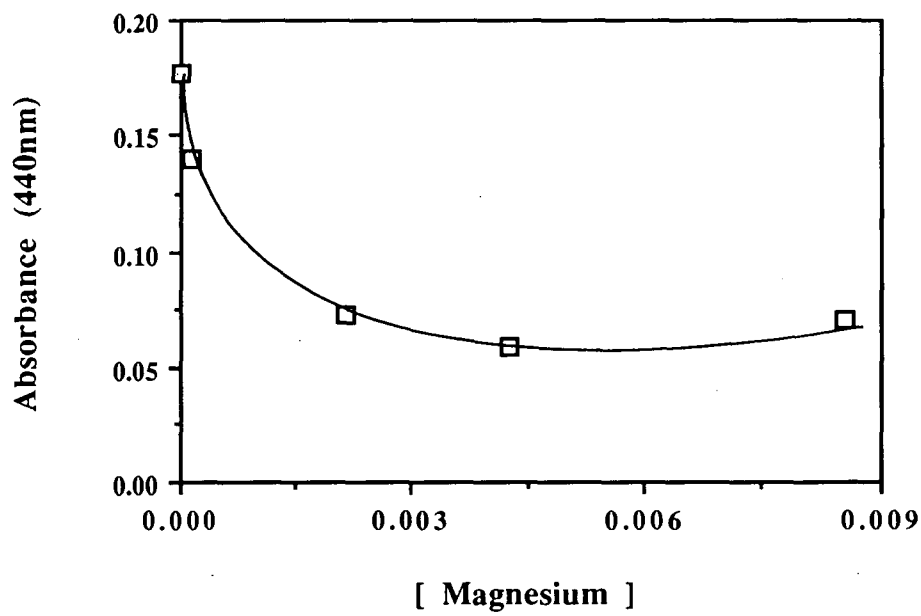

Figure 2.22 : Absorbance at 440nm of solutions containing copper for varying magnesium levels. (20°C, pH 11.0, [Cu] = 2.14×10^{-4} M, initial $[H_2O_2]$ = 0.10M, 30 min).

2.4.2 Effects of Sodium Silicate

The introduction of sodium silicate to alkaline hydrogen peroxide solutions containing copper was observed to affect the catalytic decomposition in a complex manner, with the behaviour dependent on the silicate dose employed. Figure 2.23 shows that stabilization occurred for silicate concentrations less than ~$1.5x10^{-2}$ M, with the rate of decomposition approximately halved for a concentration of ~$1.5x10^{-2}$ M which corresponded to maximum stabilization. However, further silicate addition resulted in increased rates of peroxide decomposition as shown by the increasing first-order rate constant for silicate concentrations greater than ~$1.5x10^{-2}$ M. Indeed, a ten fold increase in the rate of decomposition was observed with a silicate concentration of ~$7.5x10^{-2}$ M compared to the system with copper alone. Experiments conducted in the absence of copper resulted in little or no peroxide decomposition for all levels of silicate addition. The complex behaviour of the copper/silicate system has been reported previously[206], although no satisfactory explanation for the observed phenomena has been given.

A study of the effects of silicate addition on the absorbance of the solutions, Figure 2.24, revealed that a change in the complex species present occurred for silicate additions of greater than ~$1.5x10^{-2}$ M. The species present at low levels of silicate addition resulted in the stabilization of the system, while the increased catalytic activity observed for high levels of silicate addition was due to a second copper-silicate complex species, which can be distinguished from the first by its low absorbance characteristics. It appears that an equilibrium exists between the two catalytically active species, with high levels of silicate favouring the species which increased the rate of peroxide decomposition, while the species which gave stabilization was favoured by low silicate levels. It is interesting to note that while the addition of high levels of silicate prevented the formation of the brown copper-peroxide complex, the rate of

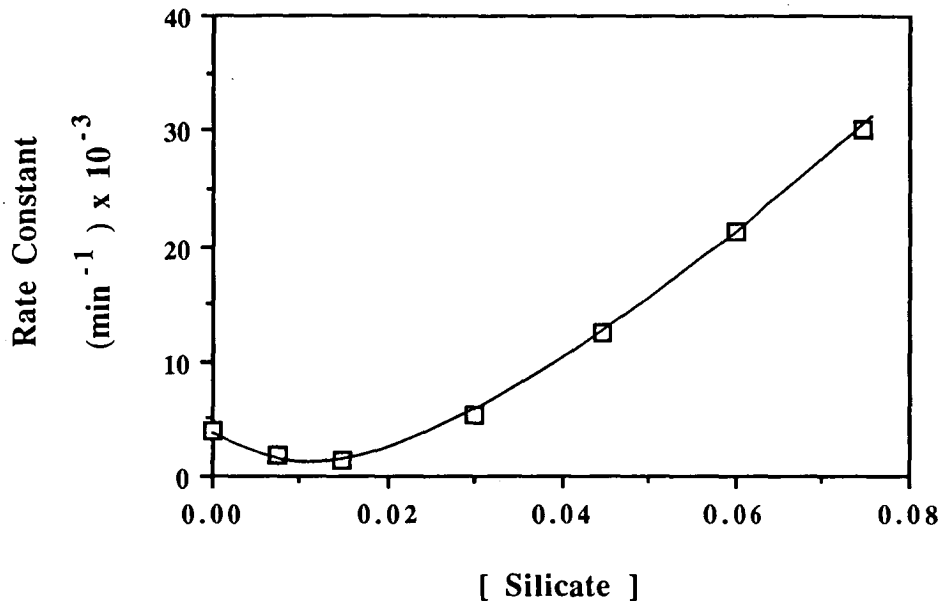

Figure 2.23 Variation in initial first-order rate constants for peroxide decomposition in the presence of copper and various levels of sodium silicate. (20°C, pH 11.0, [Cu] = 2.14×10^{-4} M, initial $[H_2O_2]$ = 0.10M).

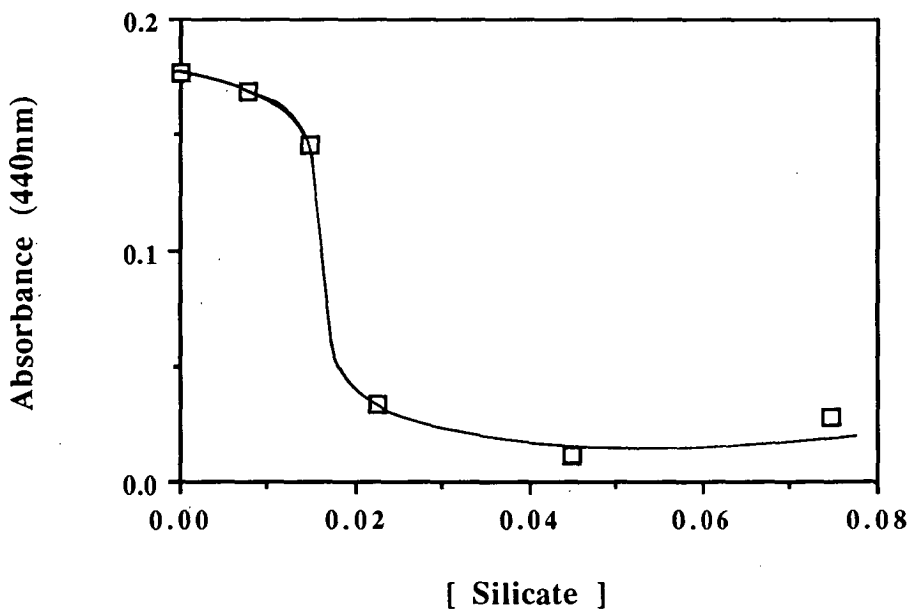

Figure 2.24 : Absorbance at 440nm of solutions containing copper for varying sodium silicate levels. (20°C, pH 11.0, [Cu]=2.14×10^{-4} M, initial $[H_2O_2]$ = 0.10M, 30 min).

peroxide decomposition was increased markedly. It has previously been reported that the coloured copper-peroxide complex is an important intermediate in the decomposition reaction, with suppression of its formation leading to decreased decomposition[69]. This may indicate that the mechanism of decomposition in the presence of copper is significantly modified in the presence of high concentrations of silicate.

The formation of mixed hydrolysis species between copper and silicate containing linkages of the type Si-O-Cu has previously been reported[199], while the complexation of copper ions with certain chelating agents has been shown to enhance the catalytic activity[37]. The increased catalytic activity has been attributed to modifications in the redox potential of the copper on complexation[41]. Taking these findings into consideration it seems reasonable to assume that mixed hydrolysis species can form between copper and silicate, with modifications in the redox potential of the copper resulting in the observed changes in the catalytic activity.

2.4.3 Effects of Aluminium and Zinc

Figure 2.25 shows the variations in first-order rate constant for peroxide decomposition in solutions containing copper and various levels of aluminium. Little change in the rate of peroxide decomposition was observed for the addition of aluminium up to a concentration of ~8.6×10^{-3} M. However, further addition up to ~2.1×10^{-2} M resulted in a significant degree of stabilization, as shown by the decreased first-order rate constant in Figure 2.25. A study of the absorbance of the solutions revealed that, for low levels of aluminium addition, there appeared to be a relatively small propensity towards formation of an aluminium-copper complex species. This is shown by the colour stability of the solutions for additions up to an aluminium concentration of ~8.6×10^{-3} M, as shown in Figure 2.26. However, further

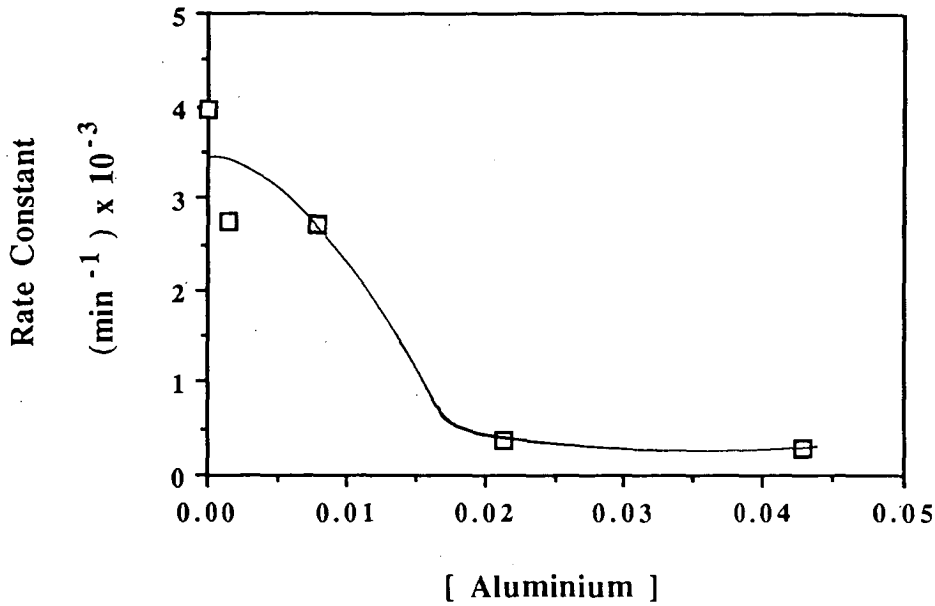

Figure 2.25 : Variation in initial first-order rate constants for peroxide decomposition in the presence of copper and various levels of aluminium. (20°C, pH 11.0, [Cu] = 2.14×10^{-4} M, initial $[H_2O_2]$ = 0.10M).

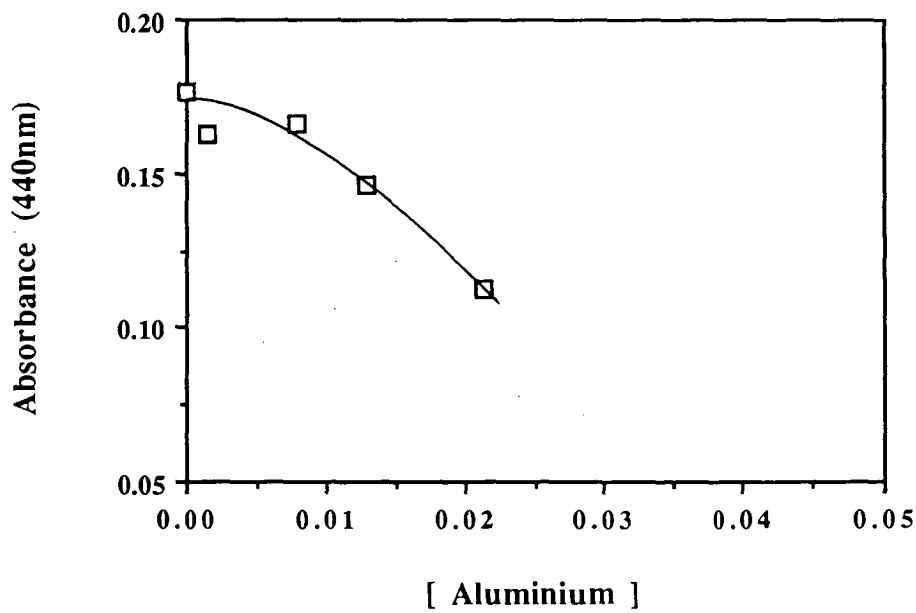

Figure 2.26 : Absorbance at 440nm of solutions containing copper and aluminium. (20°C, pH 11.0, [Cu] = 2.14×10^{-4} M, initial $[H_2O_2]$ = 0.10M, 30 min).

additions of aluminium resulted in a decrease in the absorbance, indicating that the formation of an aluminium-copper complex species occurred more readily, thus preventing the formation of the coloured copper-peroxide complex. Comparison of first-order rate constant and absorbance as the aluminium concentration was increased, Figures 2.25 and 2.26, indicates that a direct correlation exists between the development of the aluminium-copper complex species and the catalytic activity towards peroxide decomposition.

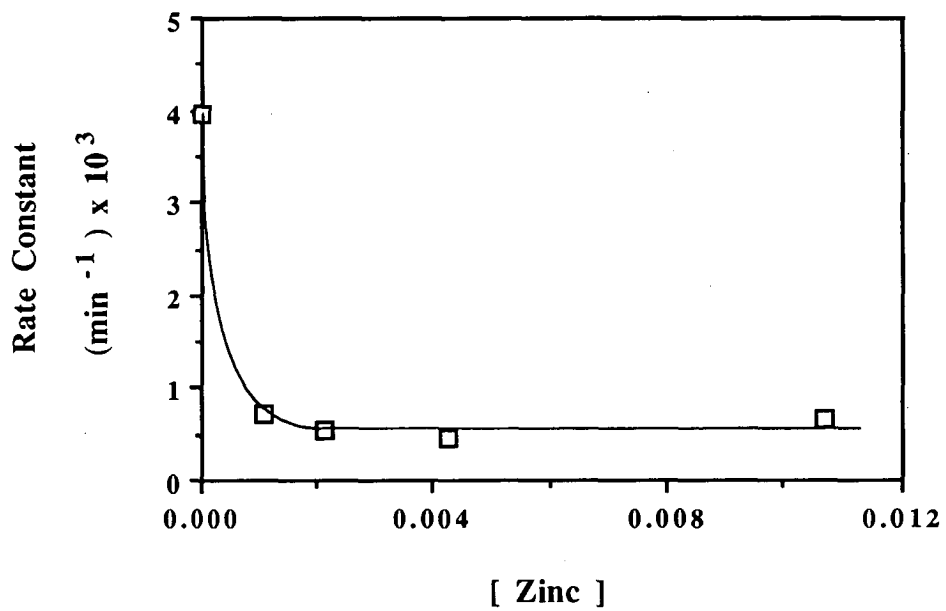

Figure 2.27 : Variation in initial first-order rate constants for peroxide decomposition in the presence of copper and various levels of zinc. (20°C, pH 11.0, [Cu] = 2.14×10^{-4} M, initial $[H_2O_2] = 0.10$M).

Figure 2.27 shows that improved stability of alkaline hydrogen peroxide in the presence of copper can be obtained with the addition of zinc. Maximum stabilization, corresponding to a minimum first-order rate constant, was found for a zinc concentration of $\sim 2.1 \times 10^{-3}$ M, with further addition of zinc giving no further

improvement. Difficulties were experienced in measuring absorbance spectra of the solutions due to a thick, white colloidal suspension which formed immediately upon addition of zinc. However, visual inspection of the solutions revealed that the intensity of the brown colouration attributed to the copper-peroxide complex was greatly diminished by the addition of increasing levels of zinc.

2.4.4 Effects of Sodium

Addition of sodium nitrate to hydrogen peroxide solutions containing copper had virtually no effect on the rate of peroxide decomposition, as shown in Figure 2.28. Similarly, very little change in the absorbance was observed as the sodium concentration was increased, Figure 2.29. The lack of influence on the catalytic properties of the copper was not unexpected as strong coupling of Cu-O-Na centres was not anticipated. Sodium was also found to have no effect on the catalytic activity of iron towards hydrogen peroxide decomposition (section 2.3.3).

2.4.5 Summary of Decomposition in the Presence of Copper

This study has shown that correlations exist between catalytic activity towards decomposition of alkaline hydrogen peroxide and the presence of complex species formed through interaction of copper and other elements such as magnesium, aluminium, silicate and zinc. The presence of such species can be followed by physical techniques such as the absorbance of the solutions, as the complexation of copper inhibits the formation of the brown copper-peroxide complex.

The addition of magnesium, zinc, aluminium or low levels of silicate were found to stabilize peroxide in the presence of copper, while the addition of high levels of silicate resulted in increased peroxide decomposition. Comparisons of the concentrations of

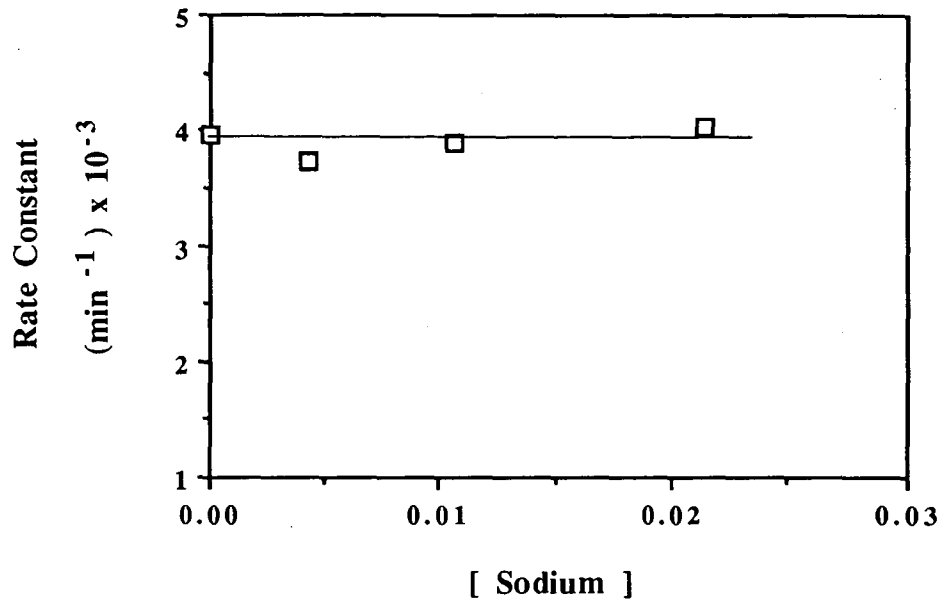

Figure 2.28 : Variation in initial first-order rate constants for peroxide decomposition in the presence of copper and various levels of sodium. (20°C, pH 11.1, [Cu] = 2.14×10^{-4} M, initial $[H_2O_2]$ = 0.10M).

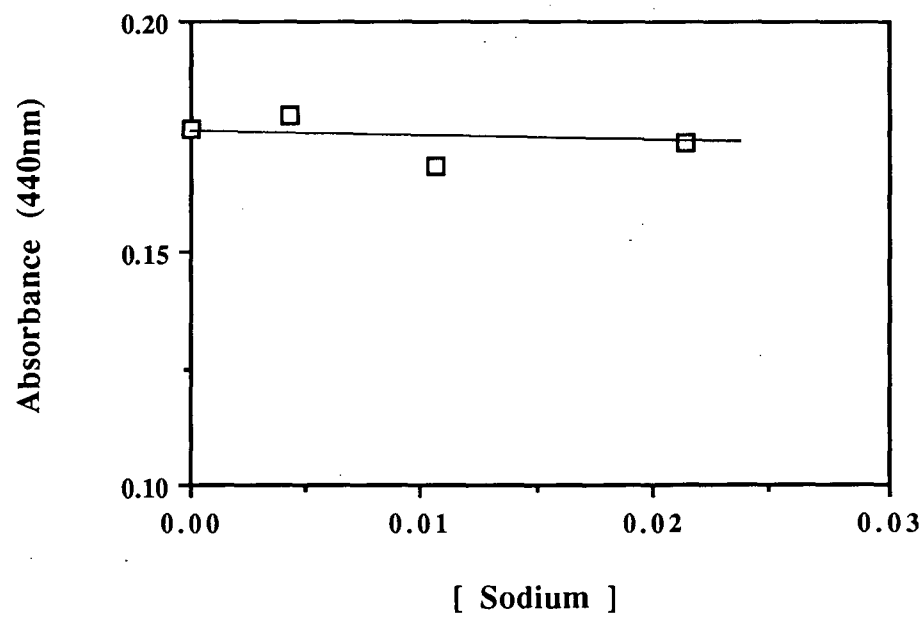

Figure 2.29 : Absorbance at 440nm of solutions containing copper for varying levels of sodium. (20°C, pH 11.1, [Cu] = 2.14×10^{-4} M, initial $[H_2O_2]$ = 0.10M, 30 min).

additives required for maximum effect reveals that zinc and magnesium have a similar propensity toward the formation of complexes with copper, while aluminium appears to have a lower affinity. In the presence of silicate it appears that two distinct copper species can be formed. At low levels of silicate addition the species present results in stabilization, while high silicate doses appear to favour the formation of a second species which gives rise to increased peroxide decomposition.

2.5 Manganese Catalysed Decomposition of Hydrogen Peroxide

A recent study by Abbot has investigated the manganese catalysed decomposition of hydrogen peroxide, together with the effects of the additives silicate, magnesium, aluminium, zinc and sodium[27]. The findings of this study, together with the results of other relevant studies, have been reviewed and summarised in order to provide a comparison with the catalytic behaviour in the presence of iron and copper.

The behaviour of manganese towards the catalytic decomposition of hydrogen peroxide has been reported to be closely related to the manganese species present[27,53]. A large number of manganese species, both soluble and insoluble, are reported to form under alkaline conditions, with different redox behaviour depending on the species present and the alkalinity[95]. The complexity of the manganese speciation present under alkaline conditions can account for the differences in behaviour towards peroxide decomposition reported by different workers, with first and second-order kinetics as well as autocatalytic behaviour observed[99,101]. There is also some confusion over the classification of the reaction as heterogeneous or homogeneous[27,35,53,70,96-98]. Solubility studies in the absence of peroxide have indicated that manganese exists entirely in insoluble form[53], while other studies have recognised that the addition of peroxide results in the dissolution of the insoluble manganese species[27,35].

The aging of manganese solutions prior to the addition of peroxide has been reported to have little effect on the subsequent peroxide decomposition reactions[25,27]. Colodette et al. found similar levels of peroxide decomposition for fresh manganese solutions and solutions containing manganese which had been aged by boiling at pH 6.5 for 3 hours[25]. Abbot allowed manganese solutions to age at 20°C and high pH levels (11.7-13.0), and found little difference in the initial decomposition reaction for fresh manganese and manganese which was aged for 24 and 48 hours[27]. The decomposition in the presence of aged manganese was found to obey first-order kinetics over the course of the reaction, whereas a deviation from first-order behaviour was observed for fresh manganese at the longer reaction times, which was attributed to decay or inhibition processes[27].

The aging of manganese at 20°C and high pH levels was found to be accompanied by the development of a brown colouration[27]. Addition of peroxide was observed to lead to the immediate dissolution of the fine precipitate which gave rise to brown colour in the solutions[27]. The intensity of the colouration, prior to the addition of peroxide, was utilized by Abbot to investigate the interaction of manganese with various additives, which was then related to the peroxide decomposition behaviour observed[27].

2.5.1 Effects of Additives

The manganese catalysed decomposition of peroxide in the presence of the additives silicate, magnesium, aluminium, zinc or sodium was found to obey first-order kinetics in all cases[27]. The rate of decomposition was found to be decreased by the addition of silicate, and to a lesser extent aluminium, while the addition of magnesium or zinc resulted in accelerated rates of decomposition[27]. Similar behaviour has been observed by a number of workers investigating the effects of silicate[25] and magnesium[26,35] on

the manganese catalysed decomposition of hydrogen peroxide. The addition of sodium was observed to have little effect on the decomposition reaction[27]. The inclusion of varying levels of these additives was also observed to influence the intensity of the brown colouration of the manganese solutions prior to the addition of peroxide[27]. This behaviour was quantified by the measurement of the absorbance of these solutions in the near uv region (350nm), and a good correlation was found between the absorbance of the solutions, which reflects the catalytic species initially present, and the catalytic activity[27].

The behaviour observed by Abbot for manganese catalysed decomposition in the presence of additives is summarised in Table 2.1, together with the results of the present study using iron and copper.

2.6 Formation of Mixed Complexes

The results of the present study investigating systems containing iron or copper have demonstrated that a correlation exists between catalytic activity and absorbance after addition of a second component which is also capable of undergoing hydrolysis in an aqueous alkaline medium. This finding is consistent with that of an analogous study of the system containing manganese reported by Abbot[27]. It can be concluded that the observed rates of catalytic peroxide decomposition depend on the species present, and it appears probable that species containing structural units of the type M_1-O-M_2 are formed (M_1 = Cu, Fe, Mn ; M_2 = Si, Mg, Al, Zn) replacing those of the type M_1-O-M_1.

Table 2.1 : Effects of Additives on the Transition Metal Catalysed Decomposition of Hydrogen Peroxide.

	Mg	Si	Al	Zn	Na
Iron	s* 1.2×10^{-3} # 6:1+	s 3.0×10^{-2} 150:1	s 1.0×10^{-2} 50:1	a 2.0×10^{-2} 100:1	n - -
Copper	s 1.3×10^{-3} 6:1	s,a $<1.5\times10^{-2}$(s) $>1.5\times10^{-2}$(a) <70:1(s) >70:1(a)	s 2.1×10^{-2} 100:1	s 1.1×10^{-3} 5:1	n - -
Manganese[27]	a 3.3×10^{-4} 15:1	s 2.2×10^{-3} 100:1	n - -	a 1.1×10^{-4} 5:1	n - -

Note : * s = stabilization, a = acceleration, n = no effect

\# Concentration of Additives (M)

\+ Additive:Metal molar ratio

Table 2.1 shows there is a wide range in the concentration of additives, or the molar ratio of transition metal:additive, required to achieve maximum response. As discussed earlier, Gilbert et al.[115] and Isbell et al.[85] have reported maximum stabilization at a ratio of 6:1 for Mg/Fe and proposed structures with this stoichiometric ratio. Higher transition metal ion to additive molar ratios have been taken as evidence

against complex formation as a mechanism for stabilization[26]. However, an alternative explanation is that the ratio of components reflects not only the stoichiometry of possible mixed complexes, but also the relative affinity for binding of M_1 and M_2 [M_1-O-M_2] through an oxygen bridge as opposed to binding with another identical centre [M_1-O-M_1] or [M_2-O-M_2]. For example, from Table 2.1, the ratio of Al/Cu for maximum stabilization is much higher than for Mg/Cu, indicating that the ease of formation decreases in the order Cu-O-Cu > Cu-O-Mg > Cu-O-Al.

The hydrolysis reactions of metal ions in isolation have been studied in great detail, and are generally well understood[207]. In contrast to this, the behaviour of systems containing two or more metal ions has received little attention, with relatively few detailed articles appearing in the literature. A series of papers by West[208-210] has reviewed the use of coprecipitation as an analytical technique for the concentration of traces from aqueous solutions, listing a wide range of metallic impurities and the agents which have been reported to be effective for their coprecipitation. The elements investigated include aluminium, copper, iron, magnesium, manganese and zinc[208-210]. However, the coprecipitation mechanism, whether adsorption, occlusion, mixed-crystal formation etc., was not discussed[208-210]. Similarly, while not dealing with the mechanisms involved, a number of studies investigating the synthesis of clay mineral structures has established the formation of coprecipitates between a wide range of metallic elements under aqueous alkaline conditions[211-213]. A number of Russian studies have also reported the coprecipitation of various combinations of elements[214-219]. Plotnikov and Safonov have studied the coprecipitation of various hydrolysable elements including Cr(III), Fe(III), Mg, Sn, Zr, Be, Sc, In, Th and Cd, and concluded that the interaction between metal ions is due to the formation of hydroxy bridges[214]. The formation of OH-bridges between iron and zirconium has also been reported by other workers[215,216]. Further reports of hydrolytic coprecipitation have been made for systems containing copper and zinc[217], iron(II) and chromium(III)[218], and

chromium(III) with zirconium and beryllium[219].

A study by Razouk and coworkers has investigated the system containing manganese and magnesium, with catalysts prepared by various techniques including coprecipitation and impregnation[35]. Electron spin resonance (esr) spectra of the various catalysts were measured in order to determine the immediate environment of the manganese[35]. The results for the coprecipitated sample indicated that the magnetic interactions between Mn^{2+} ions are small and hence the Mn^{2+} centres are widely spaced[35]. This is in contrast with the results for the sample prepared by impregnation which show stronger interactions between Mn^{2+} centres due to a higher concentration of Mn^{2+} on the surface of the catalyst[35]. The authors conclude that coprecipitation results in the manganese being fixed in the $Mg(OH)_2$ lattice[35]. Another study by Mizutani et al. into the mechanism of copolymerization of silicic acid and metal ions in aqueous media has reported the detection of bonds of the type Si-O-M by measuring the Infra-Red spectra of the coprecipitated samples[199]. These results give direct support to the concept of formation of structures of the type M_1-O-M_2.

The observation that the rate of peroxide decomposition can be either accelerated or retarded depending on the nature of M_1 and M_2 (Table 2.1) is of great importance, as any proposed mechanism for the action of additives must account for these two possible outcomes. A number of studies have attributed the stabilization of peroxide in the presence of sodium silicate or magnesium to free radical trapping mechanisms[26,102,109,113]. However, the validity of these mechanisms must be questioned as they cannot account for the accelerated rates of decomposition observed for various combinations of metals with these additives. In addition, these mechanisms do not take into consideration the correlation observed between the absorbance of solutions containing the metal catalysts in the presence of additives and the catalytic activity. This observation provides strong evidence that the additives

operate by influencing the nature of the catalytic metal species present.

Two principle mechanisms can be envisaged to account for stabilization of peroxide by the formation of mixed metal complexes between the catalytic metal ions and additives. The first mechanism involves the prevention of an interaction between the catalytic metal centre and the peroxide by the saturation of the coordination sites of the metal. It has previously been shown that the catalytic activity of chelated metals is closely related to the number of free coordination sites[37,74,75]. Supporting evidence is provided by an esr study which has established that the coprecipitation of manganese and magnesium resulted in the incorporation of manganese in the magnesium hydroxide lattice, with a resultant lowering of the surface concentration of the active catalytic centres[35]. This mechanism of stabilization would be favoured by the high ratios of additive to metal found in this study.

An alternative mechanism to explain the stabilization of peroxide by additives is the modification of the redox potential of the catalytic metal. The ability of transition metals to decompose peroxide has been shown to be closely related to their redox potentials[38,39,41,57], which can be modified by interaction with various substrates[41,57,80]. The interaction of a catalytic metal ion with a given additive to give a structural unit of the type M_1-O-M_2 may lead to a redox potential that is less favourable for peroxide decomposition leading to stabilization.

While modification of the redox potentials of catalytic metals by the interaction with additives may decrease their ability to decompose peroxide, it is also possible that the modified redox potentials will be more conducive to the decomposition of peroxide leading to accelerated rates of reaction. The likelihood that the proper modification of the redox potential of a metal ion will enhance its catalytic activity has motivated a number of studies into the effects of various supports, with increased catalytic activities observed for a number of combinations of metals and supports[38,57].

Recently, the increased catalytic activity of manganese in the presence of magnesium has been attributed to the favourable redox behaviour exhibited when the two components are present[27].

2.7 Conclusions

This study has demonstrated that correlations exist between catalytic activity towards decomposition of alkaline hydrogen peroxide and the presence of complex species formed through interaction of iron or copper and other elements such as magnesium, aluminium, silicate or zinc. The presence of such species can be followed by physical techniques such as the absorbance of the solutions. It is proposed that the catalytic activity of metal ions towards peroxide decomposition is directly related to the presence of binuclear complex species of the type M_1-O-M_2, where the individual metal ions involved and their relative molar proportions are important in determining the catalytic behaviour of the system. The formation of complex species of this type can account for both the stabilization and acceleration of metal catalysed peroxide decomposition observed in the presence of various additives.

A number of significant findings were made during the course of this study and these can be summarised as follows.

1) The iron catalysed peroxide decomposition behaviour in the absence of additives is closely related to the aging of the iron species present. Relatively high peroxide decomposition rates observed for freshly prepared solutions of Fe^{3+} can be attributed to the presence of initial hydrolysis species, while the species present following further aging are less active towards peroxide decomposition.

2) The aging of alkaline solutions of copper resulted in a decreased rate of peroxide decomposition, indicating that the hydrolysis species present following aging are less catalytically active than the initial hydrolysis species.

3) The peroxide decomposition reaction in the presence of iron or copper can be represented by first-order kinetics if the initial reaction period is considered. Deviations from first-order behaviour at greater time periods can be attributed to the aging of the catalytic species.

4) The iron or copper catalysed peroxide decomposition reactions in the presence of magnesium, silicate, aluminium, zinc or sodium can be represented by first-order kinetics over the reaction periods studied.

5) The addition of magnesium resulted in the stabilization of both the iron and copper catalysed decomposition of hydrogen peroxide.

6) Hydrogen peroxide solutions containing iron were stabilized by the addition of sodium silicate.

7) The addition of low levels of sodium silicate resulted in the stabilization of hydrogen peroxide in the presence of copper, while high levels of addition gave accelerated rates of decomposition.

8) The addition of aluminium resulted in stabilization of hydrogen peroxide in the presence of either iron or copper.

9) The presence of zinc was observed to increase the rate of iron catalysed peroxide decomposition, while stabilization was observed in the presence of copper.

10) The addition of sodium had little or no effect on the iron or copper catalysed decomposition of hydrogen peroxide.

CHAPTER 3

Solubility of Transition Metal Species and Stabilizers

3.1 Introduction

The solubility of transition metal ions has been discussed by a number of workers in relation to peroxide decomposition behaviour[24,27,35,53,96-98]. Studies have shown that the form in which transition metals exist can be related to their ability to catalytically decompose peroxide, both in the presence[18,19,22] and absence[24,27,35,53] of pulp. Changes in the form of transition metals through processes such as aging[27,53], chelation[21,37,41,73-75] or supporting on various substrates[56,57,62] have been reported to have a significant bearing on the catalytic activity in the absence of pulp. In the presence of pulp, metals are thought to exist as pulp-metal complexes in equilibrium with free metal ions in solution[11,18,20]. Metals which are loosely complexed by the pulp, and thus easily solubilized, are thought to be active peroxide decomposition catalysts, while those which are strongly complexed are thought to be inactive[9,18,22].

Under alkaline conditions, metals in ionic form are expected to be rapidly converted to non-ionic species[149]. A recent study investigating the solubility of aged samples of the transition metals iron, copper and manganese using ultrafiltration has reported that these metals exist entirely in insoluble forms in aqueous alkaline solutions[53]. However, a number of studies have found that the addition of hydrogen peroxide can result in significant changes in the solubility of transition metals in alkaline solutions[27,35,45]. For example, the complete dissolution of the solid manganese species formed on the addition of alkali to manganese salts is reported to occur on the addition of peroxide[27,35], while precipitated $Fe(OH)_3$ has also been reported to dissolve on the addition of peroxide in the presence of EDTA[45].

The introduction of various additives has also been reported to influence the solubility behaviour of transition metal ions[24,25,35]. For example, silicate, citrate and tartrate

ions are reported to form complexes with heavy metal cations and maintain these ions in solution[24]. In contrast, the addition of magnesium hydroxide has been reported to result in the precipitation of transition metals such as copper[24] and manganese[35]. A recent study has shown that the addition of silicate does not result in the solubilization of aged metal ion species, ie. species already in insoluble form[25]. This indicates that the effect of silicate addition on the solubility behaviour is dependent on the actual metal species initially present.

The presence of pulp may be expected to further complicate the solubility behaviour in alkaline peroxide systems. Pulp has been reported to act as a cation exchanger, with the formation of pulp-metal ion complexes of varying stability, depending on the individual metal ions[11]. Iron, in particular, has been reported to form strong interactions with the cellulose components of pulp[22,127,182], while manganese has been found to be loosely bound to pulp[18,22]. In addition, the complexation of metal ions by soluble by-products of bleaching reactions has been reported, with the resulting soluble catalytic species believed to be highly active towards peroxide decomposition[115].

The solubility behaviour of freshly prepared samples of the transition metals iron, copper and manganese, both individually and in combination with the additives sodium silicate and magnesium, has been examined in the presence and absence of chelated *P. radiata* TMP. The results can be compared with the solubility behaviour of the naturally occurring transition metal ions present in the *P. radiata* TMP. Samples of the respective liquors were obtained at various reaction times, filtered using a 0.45 μm syringe filter, and analysed for transition metal ions using atomic absorption. The level of silicate employed was 0.033 M (~5% SiO_2 on o.d. pulp) while a dose of ~2.5% magnesium nitrate on pulp (3.9×10^{-3} M Mg) was used, as a corresponding dose has been reported to give significant effects during the bleaching of pulp[167].

Transition metals were added as the nitrate salts, with the following concentrations being employed: [Fe] = 3.56×10^{-5} M, [Cu] = 6.40×10^{-5} M and [Mn] = 3.71×10^{-5} M. A reaction temperature of 50°C was employed, with the pH maintained at a constant level of 11.0 in each case. A low pulp consistency (4%) was utilized to enable continuous mixing over the duration of the reaction, and to facilitate the maintenance of the constant pH. The results obtained from identical experiments conducted in the absence of peroxide have been included for comparison.

3.2 Solubility of Additives

In order to interpret the effects of the additives sodium silicate and magnesium on the solubility of transition metal ions it was first necessary to determine the solubility of the additives themselves.

Figure 3.1 shows the solubility of magnesium at pH 11.0 in the presence and absence of pulp. In the absence of pulp, magnesium was found to exist entirely in an insoluble form, presumably as precipitated magnesium hydroxide. A similar study by Burton has reported that severe precipitation occurred following the addition of sodium hydroxide and hydrogen peroxide to solutions containing magnesium, indicating that an insoluble species was formed[28]. The inclusion of pulp was found to result in the partial solubilization of the added magnesium, with increased levels of soluble magnesium observed as the reaction progressed, as shown in Figure 3.1. The presence of peroxide appeared to have little effect on the observed solubility behaviour. Clearly the presence of pulp has a significant influence on the solubility of the added magnesium. Experiments conducted in the absence of added magnesium indicated that the naturally occurring magnesium present in the pulp was only solubilized to a minor extent.

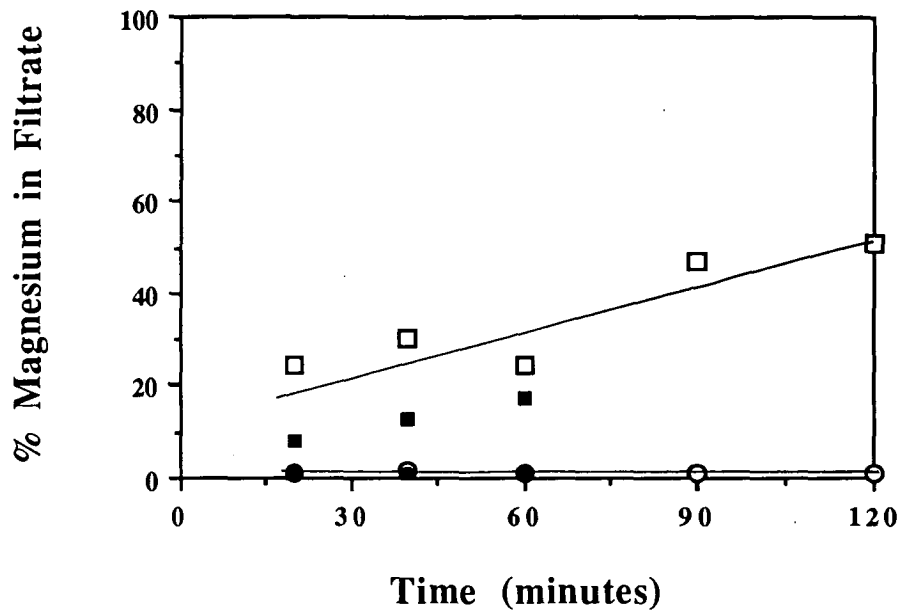

Figure 3.1 : Solubility of added magnesium in the presence (□) and absence (○) of chelated TMP. (50°C, pH 11.0, 4% consistency ; open symbols : initial $[H_2O_2]$ = 0.035M, filled symbols : no H_2O_2).

Sodium silicate was found to exist almost exclusively in a soluble form both in the presence and absence of pulp under the conditions used in the present study, as shown in Figure 3.2. The nature of the silicate species present under the conditions utilized for peroxide bleaching has previously been discussed by a number of workers[195-198]. The stabilizing ability of silicate has been attributed to its ability to form insoluble heavy metal silicates[15,25], and it has been shown that the addition of silicate does not result in the solubilization of insoluble forms of transition metals[25]. In contrast, the results obtained from studies conducted in the presence of pulp have indicated that considerable percentages of the silicate may remain in a soluble form. Kutney and Evans reported that 52% of the original sodium silicate remained in the spent bleach liquor[140], while Graham et al. reported that 95% of the silicate was washed away when brightened pulp was drained to make a handsheet[161]. A recent investigation by Burton found that the degree of precipitate formation in peroxide bleaching liquors was

dependent on the order of addition of the various components[28]. Using the order of addition employed in the current study, silicate added first followed by sodium hydroxide and finally peroxide, Burton reported that only slight precipitation occurred, even though the conditions were designed to be a severe test for precipitate formation[28].

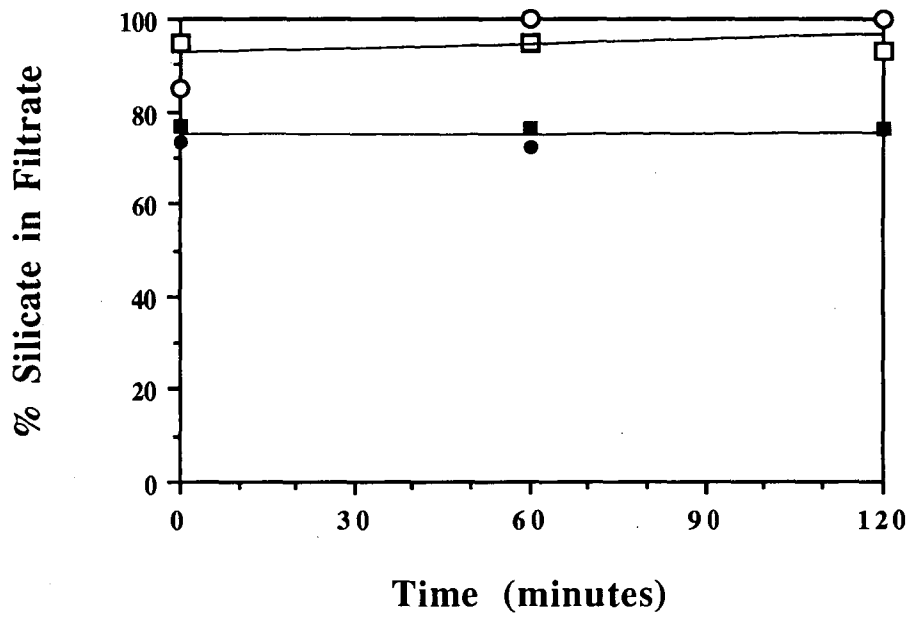

Figure 3.2 : Solubility of added silicate in the presence (□) and absence (○) of chelated TMP. (50°C, pH 11.0, 4% consistency ; open symbols : initial $[H_2O_2]$ = 0.035M, filled symbols : no H_2O_2).

3.3 Solubility of Added Iron

In aqueous solutions iron is known to undergo hydrolysis and polymerization reactions, and these reactions have been studied in considerable detail at low pH[174-178]. The hydrolysis of inorganic Fe(III) solutions has been reported to consist of several steps: (1) formation of low molecular weight species; (2) formation of a red cationic polymer; (3) aging of the polymer, with eventual conversion to oxide phases;

and (4) precipitation of oxide phases directly from low molecular weight precursors[171]. A wide range of iron species may be formed as a result of these hydrolysis reactions, with the attainment of equilibrium occurring very slowly, even requiring weeks or months[171-178]. However, the rate of the hydrolysis reaction, or the degree of aging, has been reported to be accelerated by heating or raising the pH of the iron solutions[127]. Under the conditions typically used in peroxide bleaching formulations iron may be expected to be rapidly converted into non-ionic species[53,149]. A recent study of the solubility of an "aged" solution of iron found that ~100% of the iron was in an insoluble form[53].

The solubility of freshly prepared iron at pH 11.0 in the absence of pulp is shown in Figure 3.3. The majority of the iron in the present study was found to be in a soluble form, implying that the hydrolysis reactions responsible for aging occur slowly under the conditions employed. The slow nature of the hydrolysis reaction was evident through the eventual formation of a brown colloidal precipitate over a period of days in samples of the filtrates. Figure 3.3 also demonstrates that the majority of iron exists in a soluble form in the presence of sodium silicate. In contrast, the addition of magnesium resulted in the formation of an insoluble iron species. This result clearly demonstrates that an interaction occurs between iron and magnesium, as postulated earlier to account for observed peroxide decomposition behaviour (see section 2.3.1). It is also apparent from Figure 3.3 that the presence of peroxide had little effect on the solubility behaviour of iron in the absence of pulp.

Figure 3.4 shows the solubility of added iron in the presence of chelated *P. radiata* TMP. While the inclusion of pulp appeared to have little effect on the solubility of iron in the presence of silicate, significant changes were observed in the presence of pulp for the systems containing iron alone, and in combination with magnesium. In the presence of pulp the solubility of iron was found to be significantly lower than under

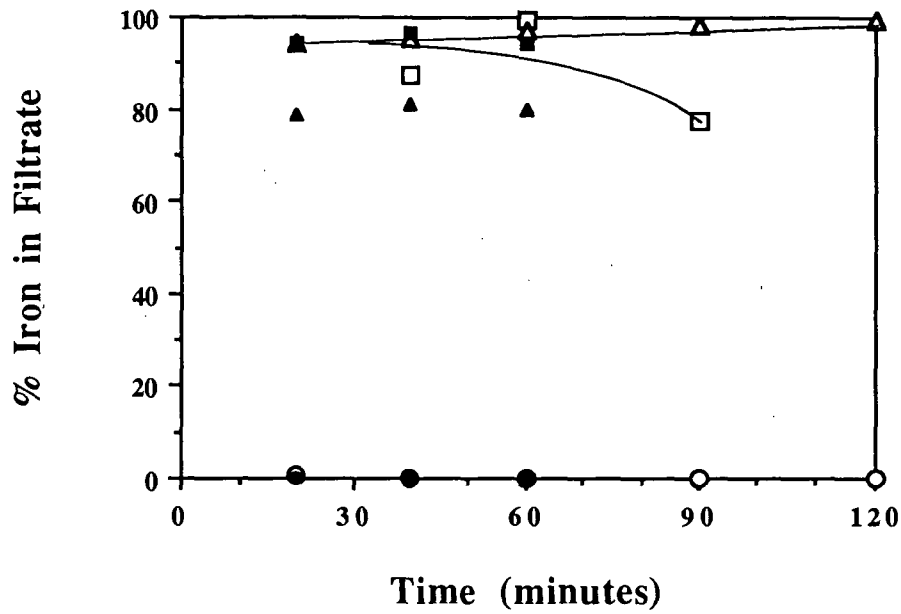

Figure 3.3 : Solubility of iron in the absence of pulp. (50°C, pH 11.0 ; open symbols : initial $[H_2O_2]$ = 0.035M, filled symbols : no H_2O_2 ; □ : Fe alone, △ : Fe+Si, ○ : Fe+Mg).

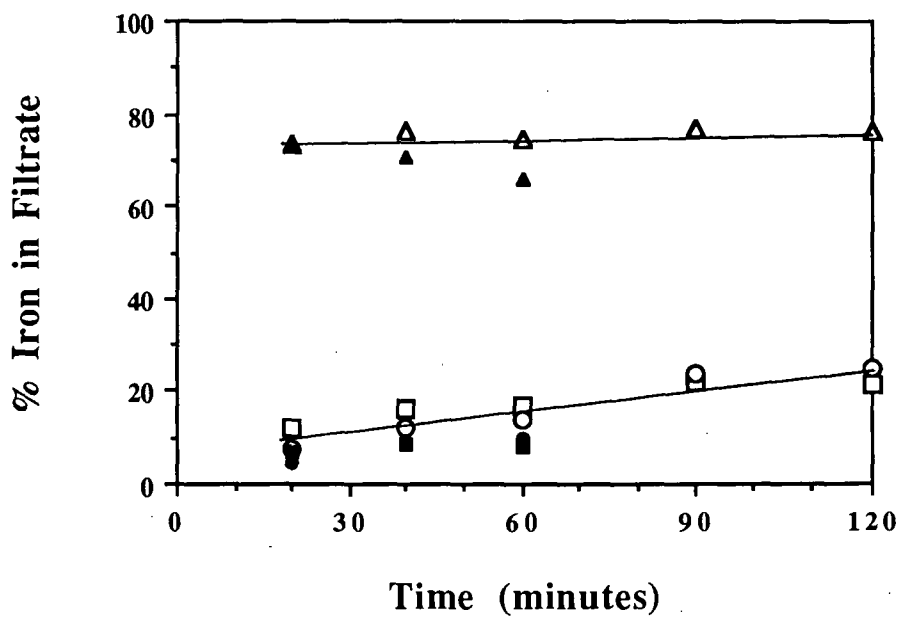

Figure 3.4 : Solubility of added iron in the presence of chelated TMP. (50°C, pH 11.0, 4% consistency ; open symbols : initial $[H_2O_2]$ = 0.035M, filled symbols : no H_2O_2 ; □ : Fe alone, △ : Fe+Si, ○ : Fe+Mg).

identical conditions in the absence of pulp. Iron has previously been reported to have a high affinity for binding to mechanical pulp[127], particularly the cellulose component[182]. It is likely that the interaction of iron with various components of the pulp are responsible for the decreased solubility observed compared with that in the absence of pulp. In the presence of magnesium the solubility of iron was increased by the inclusion of pulp. The solubilizing effects of organic by-products of bleaching have previously been reported for the system containing iron and magnesium[115]. Therefore, it seems likely that the change in the solubility behaviour observed for the iron/magnesium system in the presence of pulp is due to the interaction of the metal species with soluble organic components derived from the pulp. The increase in solubility over the course of the reaction observed in the present study supports the concept of interaction between the metal species and soluble products from reactions of the pulp with either peroxide or alkali. As was observed in the absence of pulp, the presence of peroxide had little influence on the solubility behaviour of iron in the presence of chelated TMP.

3.4 Solubility of Added Copper

The addition of hydrogen peroxide to alkaline solutions containing copper has previously been reported to lead to the immediate formation of a brown colouration, attributable to a copper-peroxide species[68,69,88]. In the present study the filtration of a solution containing the brown copper-peroxide species, which formed on the addition of peroxide, yielded a clear, colourless solution. Figure 3.5 shows that a minimal percentage of the added copper was found in the filtrate, demonstrating that the predominant copper species present following the addition of peroxide was insoluble. The addition of alkali to a copper solution in the absence of peroxide did not result in the development of a brown colouration. However, the low level of copper found in the filtrate from this solution, Figure 3.5, suggests that the copper was also

predominantly in an insoluble form.

The addition of magnesium was observed to have little effect on the solubility of copper in the absence of pulp, as shown by the low level of the metal found in the filtrate in Figure 3.5. However, in the presence of sodium silicate a large proportion of the copper was maintained in the solution, Figure 3.5. The solubilizing effects of sodium silicate via the formation of silicate-heavy metal complexes have been reported previously by Nicoll and Smith[24]. In contrast, the results of a series of ultrafiltration experiments by Colodette et al. suggested that sodium silicate did not solubilize transition metals to any great extent[25]. This apparent contradiction can be explained by considering the form of the initial metal species prior to the addition of silicate. In the latter study by Colodette et al. the metals were in an "aged" form prior to the addition of silicate[25]. In this form the metals have previously been demonstrated to be insoluble[53]. In contrast, the condition employed in the present study, and also in the study by Nicoll and Smith[24], allowed the silicate to come into contact with the metals prior to the formation of insoluble species. Therefore, it seems reasonable to assume that the interaction of silicate with metals such as copper can prevent the hydrolysis reactions which lead to the formation of the insoluble species. However, if the metals are already in an insoluble form the addition of silicate cannot lead to their solubilization.

It has previously been demonstrated that the addition of sodium silicate resulted in the modification of the copper catalysed peroxide decomposition behaviour (see section 2.4.2). A correlation observed between the catalytic activity and the absorbance of the copper solutions as the level of silicate was increased suggested that the formation of new copper-silicate complex species was important in determining the catalytic behaviour (see section 2.4.2). The results obtained in the current study demonstrate that the addition of silicate had a significant influence on the solubility of added copper,

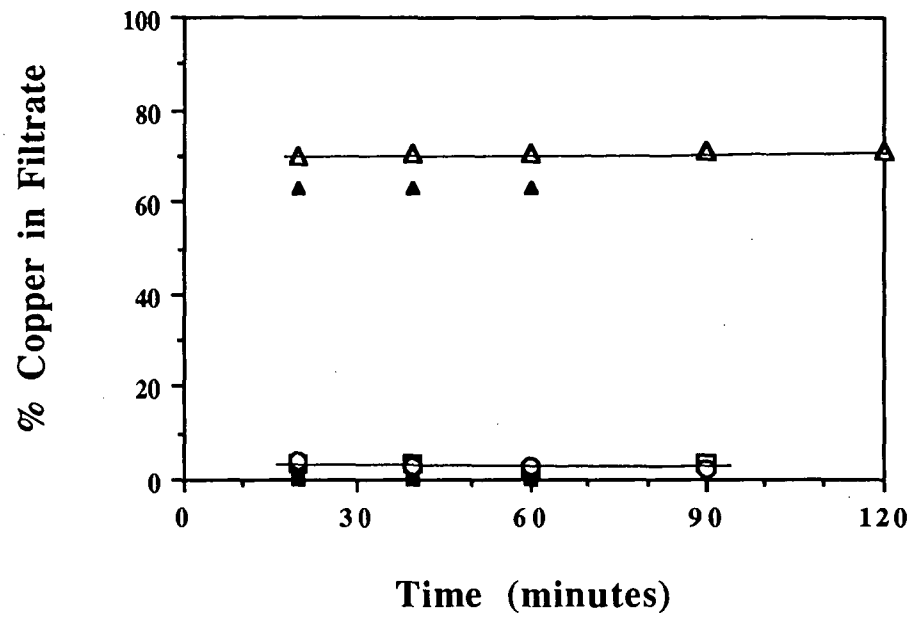

Figure 3.5 : Solubility of copper in the absence of pulp. (50°C, pH 11.0 ; open symbols : initial $[H_2O_2]$ = 0.035M, filled symbols : no H_2O_2 ; □ : Cu alone, △ : Cu+Si, ○ : Cu+Mg).

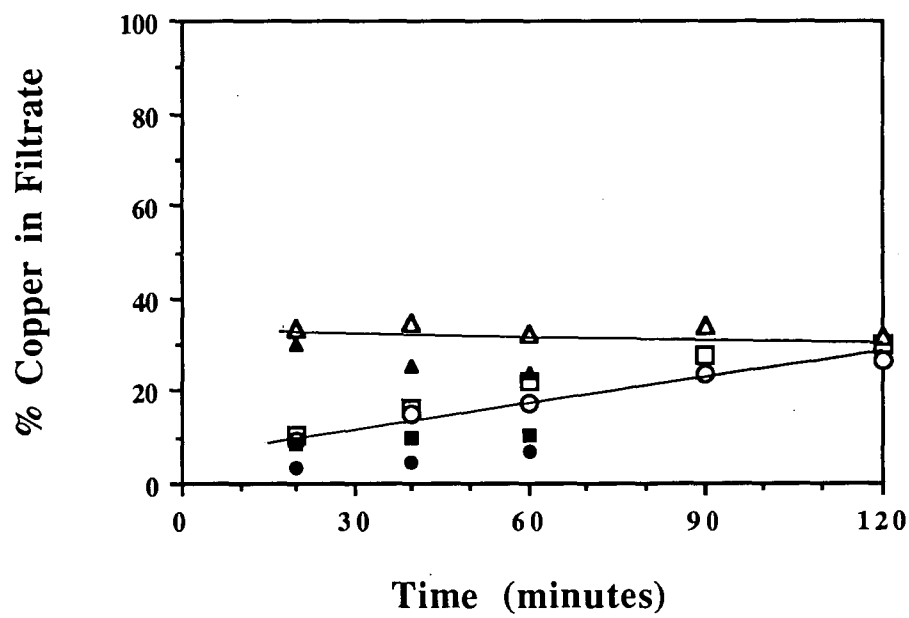

Figure 3.6 : Solubility of added copper in the presence of chelated TMP. (50°C, pH 11.0, 4% consistency ; open symbols : initial $[H_2O_2]$ = 0.035M, filled symbols : no H_2O_2 ; □ : Cu alone, △ : Cu+Si, ○ : Cu+Mg).

providing further evidence supporting the proposed formation of a copper-silicate complex species.

As was observed for iron, the inclusion of pulp had a significant effect on the solubility behaviour exhibited in the presence of copper, as shown in Figure 3.6. In the presence of chelated TMP the solubility behaviour of copper was found to be similar in the presence and absence of magnesium, with an increase in solubility observed over the duration of the reaction. Under identical conditions in the absence of pulp, copper was found to be entirely in an insoluble form, as shown in Figure 3.5. The observed variation in behaviour indicates that the metal species may interact with soluble components from the pulp to give soluble copper species. Comparison with Figure 3.5 also reveals that the inclusion of pulp resulted in a lowering of the proportion of copper that was maintained in a soluble form following the addition of sodium silicate. This suggests that the pulp may compete with silicate to form copper complexes, with the binding of copper to insoluble pulp components leading to the observed lower solubility. It should be noted that the solubility of copper was still observed to be higher in the presence of silicate than in its absence.

The solubility of copper was found to be similar in the presence and absence of peroxide for systems studied in solution and in the presence of pulp. A similar finding was observed for the solubility of iron in section 3.3.

3.5 Solubility of Added Manganese

The speciation of manganese present in aqueous alkaline solutions has been reported to be extremely complex, with insoluble species including $Mn(OH)_2$, MnO, Mn_3O_4, MnOOH, Mn_2O_3 and MnO_2, together with soluble Mn(II) and Mn(III)[95]. The relationship between the solubility of the manganese species present and the

decomposition of peroxide has been discussed by a number of workers[35,53,96,97]. Broughton and Wentworth reported that the addition of manganous salts to a peroxide solution gave no decomposition until the addition of sufficient alkali to produce a brown colloidal precipitate[97]. Colodette et al. determined that manganese was essentially 100% insoluble at pH values of 9.8, 10.8 and 11.8 in the absence of peroxide and concluded that manganese dioxide is the most likely active species present[53]. However, the correlation between the solubility of the manganese species and the catalytic activity is complicated by the reported dissolution of solid manganese species in the presence of hydrogen peroxide[27,35]. The complete dissolution of the solid manganese species formed on the addition of alkali to manganese salts is reported to occur on the addition of peroxide[27,35].

The solubility of freshly prepared manganese in the absence of pulp is shown in Figure 3.7. In the presence of either magnesium or sodium silicate, the solubility behaviour appeared to follow the trends previously observed for iron and copper. The manganese was found to exist solely in an insoluble form in the presence of magnesium, whereas in the presence of silicate a significant proportion of the manganese was retained in solution. In the absence of additives the solubility of manganese was found to vary considerably over the course of the reaction. In the absence of peroxide the solubility of manganese dropped sharply over the early stages of the reaction. In contrast, the majority of the manganese was found to exist in a soluble form in the presence of peroxide. However, following the complete decomposition of peroxide the solubility was found to decrease markedly, as shown by the sample withdrawn after 120 minutes. Similar results have been obtained by a number of workers investigating the relationship between the solubility of manganese and the concentration of peroxide[27,35,98].

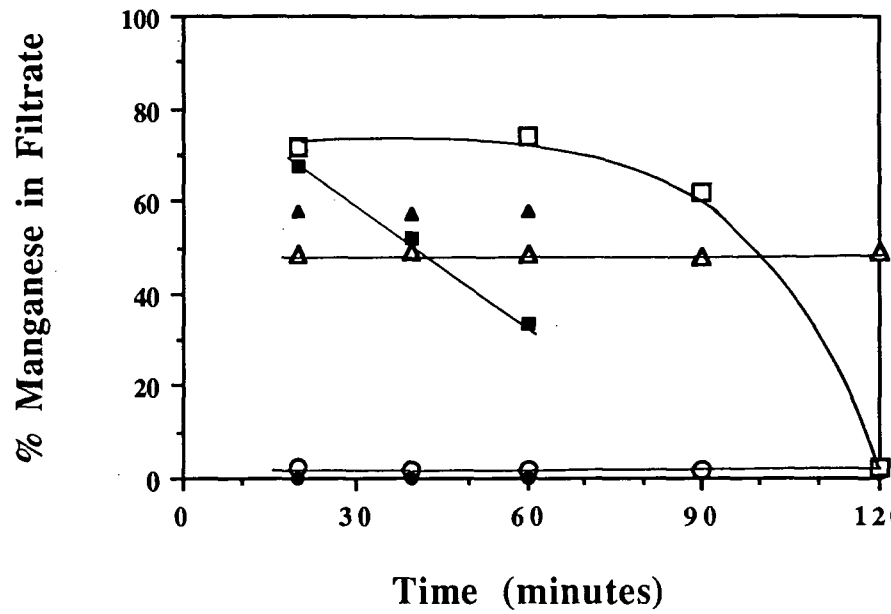

Figure 3.7 : Solubility of manganese in the absence of pulp. (50°C, pH 11.0 ; open symbols : initial $[H_2O_2]$ = 0.035M, filled symbols : no H_2O_2 ; □ : Mn alone, △ : Mn+Si, ○ : Mn+Mg).

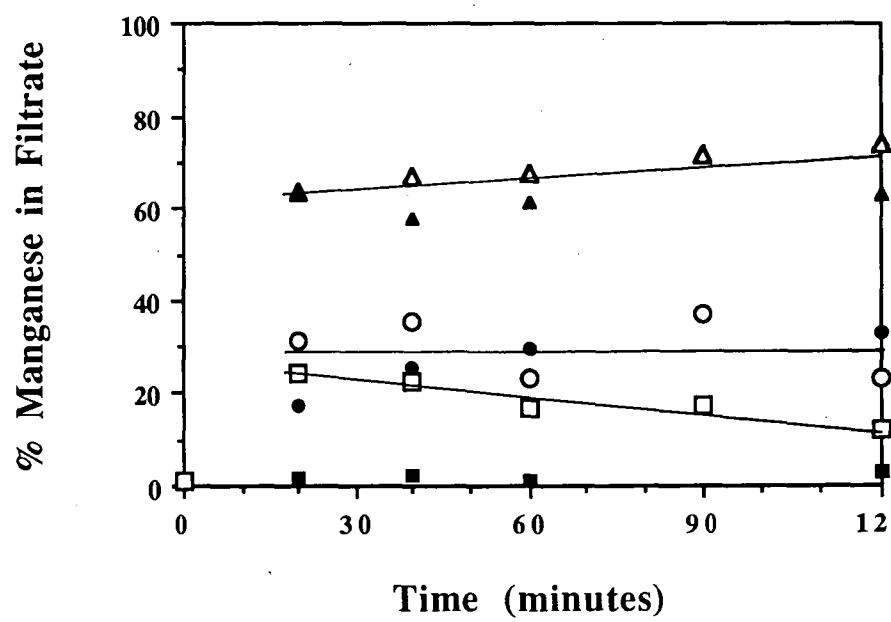

Figure 3.8 : Solubility of added manganese in the presence of chelated TMP. (50°C, pH 11.0, 4% consistency ; open symbols : initial $[H_2O_2]$ = 0.035M, filled symbols : no H_2O_2 ; □ : Mn alone, △ : Mn+Si, ○ : Mn+Mg).

The solubility of added manganese in the presence of pulp is shown in Figure 3.8. Again, the behaviour observed for manganese in the presence of additives resembled that observed for iron and copper in the presence of pulp, with silicate maintaining a significant percentage of the manganese in solution, while the solubility in the presence of magnesium increased over the course of the reaction. The solubility of manganese alone in the presence of pulp was found to be dependent on the level of peroxide present, as demonstrated by the decrease in solubility observed as the peroxide concentration declined over the course of the reaction. This dependence is also clearly demonstrated by the low solubility of manganese observed at pH 11.0 in the absence of peroxide, as shown in Figure 3.8.

3.6 Solubility of Naturally Occurring Transition Metals During the Bleaching of TMP

The majority of studies investigating the form of naturally occurring transition metal ions present in mechanical pulps have focused on their response to pre-treatments such as chelation or acid washing prior to bleaching[2,18,22,23,127]. It is generally recognised that pulp acts as a weak cation exchanger, with differing affinities towards binding to individual transition metals[11,18,20]. Under the conditions employed using chelating agents two equilibria have been recognised as being important[11], and these may be represented as follows:

pulp-metal ion complex

free metal ions in solution

chelating agent-metal ion complex

Clearly the degree of solubilization of the metals present in the pulp during chelation will be dependent on the relative stabilities of the respective pulp-metal and chelating agent-metal complexes, with a low stability of the former coupled with a high stability of the latter favouring the removal of the metals[11].

3.6.1 Effects of Chelation on the Transition Metal Content of TMP

Table 3.1 shows the effects of chelation and washing on the transition metal ion content of the *P. radiata* TMP used in the current study. The relative levels of the transition metals present in the unchelated TMP are in good agreement with those reported recently for a series of samples of *P. radiata* wood obtained from various locations in Australia[122]. Manganese was found to be present in the highest level in the original TMP and was also the most readily removed by the chelation process. Similar findings regarding the effects of chelation on the manganese content of mechanical pulp have been reported by many workers[9,18,22,106,127]. It is apparent that manganese is loosely complexed to the pulp and thus is easily solubilized on the addition of the chelating agent DTPA.

In contrast to the behaviour observed for manganese, iron was present in a much lower quantity in the original TMP and was not removed to any great extent following chelation with DTPA and washing, Table 3.1. This observation was not surprising as iron has previously been reported to form strong bonds with the cellulose component of mechanical pulps[127,182], particularly under the conditions which exist during the manufacture of thermo-mechanical pulps[2]. A number of previous studies have also reported that chelation with DTPA was inefficient in removing iron from mechanical pulps[9,18,22,127].

Table 3.1 : Effects of Chelation with DTPA on the Transition Metal Content of the *P. radiata* TMP used in the current study.

Pulp Type	Transition Metal Content (ppm)		
	Fe	Mn	Cu
TMP	12.0	39.9	6.2
Chelated TMP	10.3	4.0	3.5

Copper was found to be the least abundant of the three major transition metal, peroxide decomposition catalysts present in the original TMP, as shown in Table 3.1. Chelation with DTPA and washing was found to lead to a reduction in the level of copper by approximately 50%. It has previously been demonstrated that the chelation of TMP results in the removal of the copper which is accumulated during the pulping process, but not the copper derived from the wood source[22]. This suggests that the naturally occurring copper contained in the *P. radiata* TMP used in the present study is derived approximately equally from the wood and from the processes involved in the production of the pulp. This assertion is supported by a recent study which found the concentration of copper in a number of *P. radiata* wood samples to be of the order of 1-2 ppm[122].

In contrast to the considerable quantity of data which has been reported describing the effects of chelation on the transition metals present in mechanical pulps, much less is known about the solubility behaviour of the metal ions during peroxide bleaching reactions. The results presented in the previous sections of this study have

demonstrated that the presence of pulp can have a significant influence on the solubility behaviour of added samples of freshly prepared transition metals, both in the presence and absence of stabilizers. Therefore, in order to gain more information about the naturally occurring metal species present in the original TMP, their solubility behaviour was examined during a series of bleaching reactions.

3.6.2 Solubility of Naturally Occurring Iron

Figure 3.9 shows that the presence of peroxide had little effect on the solubility behaviour of the naturally occurring iron under alkaline conditions (pH 11.0). A small, but significant percentage of the naturally occurring iron was found to be solubilized during the bleaching of TMP in the absence of additives. The addition of magnesium nitrate was observed to have little effect on this solubility behaviour. However, with the addition of sodium silicate the solubility of iron was found to be dramatically increased. Approximately 60% of the original iron was found to be present in the filtrate for a level of silicate addition of ~0.033M, which corresponds to ~5% SiO_2 on pulp. Analysis of the iron content of bleached pulp samples obtained at the completion of reactions in the presence of silicate revealed a corresponding drop in the level of iron which remained with the pulp, as shown in Table 3.2.

Table 3.2 : Effects of Bleaching TMP in the Presence of ~5% Sodium Silicate on the Iron Content of the Pulp.

Pulp Type	Iron Content (ppm)
Untreated TMP	12.0
Bleached TMP (added Silicate)	5.1

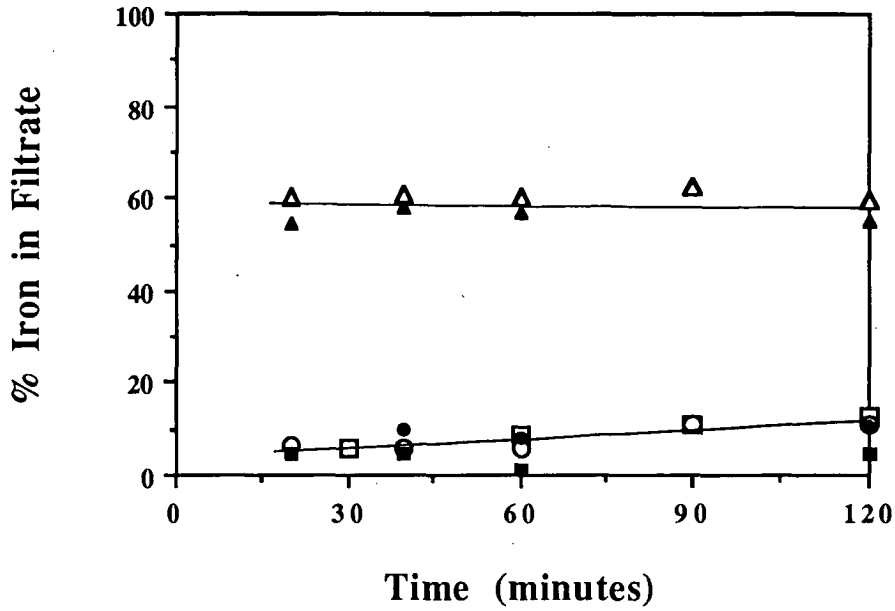

Figure 3.9 : Solubility of the naturally occurring iron from TMP. (50°C, pH 11.0, 4% consistency ; open symbols : initial $[H_2O_2]$ = 0.035M, filled symbols : no H_2O_2 ; □ : Fe alone, Δ : Fe+Si, O : Fe+Mg).

It is interesting to note that the amount of iron which was solubilized during bleaching in the presence of silicate exceeded that which could be removed by chelation with DTPA prior to bleaching, Table 3.1. A similar decrease in the iron content which was bound to pulp has been reported for the peroxide bleaching of a bagasse chemical pulp in the presence of sodium silicate[220]. In the absence of silicate, little of the iron was found to be solubilized, while increasing silicate doses resulted in increasing degrees of iron solubilization, with the iron content of the bleached pulps observed to decrease by ~50% using silicate doses in excess of 4% on pulp[220].

Many previous studies investigating the nature of the transition metals present in mechanical pulps have concluded that the majority of the iron is tightly bound to the pulp, as it is only removed to a minor extent by chelation[9,18,22,127,182]. This has led to the proposal that the iron present is in an aged form[22], as in this form iron has been

shown to bind tenaciously to pulp[22,127,182]. A recent study has shown that the addition of sodium silicate does not result in the solubilization of the aged form of iron[25]. However, the present study has clearly demonstrated that the addition of silicate does result in solubilization of the naturally occurring iron present in *P. radiata* TMP to a major extent. Therefore, it seems that the naturally occurring iron present in the TMP cannot be satisfactorily represented by the aged iron species used previously to simulate its catalytic behaviour during bleaching[25].

The solubility behaviour of the naturally occurring iron present in TMP can be compared with that observed previously for freshly prepared iron in the presence of chelated TMP (see section 3.3). The similarities in the observed behaviour, particularly the increased solubility in the presence of sodium silicate, indicates that it is not possible to distinguish between these two sources of iron on the basis of their solubility characteristics. However, it has previously been reported that freshly prepared iron does not form strong interactions with pulp, as it is removed quite readily by washing with HCl[127]. It is unlikely then that the naturally occurring iron, which was only removed to a minor extent by chelation with DTPA, is in a form identical to that produced following the addition of freshly prepared iron to pulp. This is highlighted in Table 3.3, which demonstrates that while washing alone did not remove a significant proportion of iron which had been added to pulp in either fresh or aged form, treatment with DTPA resulted in the removal of the majority of the freshly prepared iron, but had little effect on the level of aged iron which remained attached to the pulp.

It is apparent that the naturally occurring iron present in the *P. radiata* TMP used in the current study cannot be adequately represented by either freshly prepared or aged iron samples. The original iron species was found to be tightly bound to the pulp, as it was not removed to a great extent by chelation, and yet was solubilized to a large degree

under the conditions which prevailed during bleaching in the presence of sodium silicate.

Table 3.3 : Effect of washing or chelation on the retention of added iron in the presence of pre-chelated *P. radiata* TMP.

Pulp Treatment	Iron Content (ppm)	
	Fresh Fe	Aged Fe
Washing	59.5	53.2
Chelation	23.1	53.6

3.6.3 Solubility of Naturally Occurring Copper

The concentration of naturally occurring copper present in the *P. radiata* TMP was found to be too low to allow the accurate determination of its solubility behaviour during peroxide bleaching treatments.

3.6.4 Solubility of Naturally Occurring Manganese

A number of studies has demonstrated that the manganese present in mechanical pulps originates predominantly from the wood source[18,22,127]. Its ease of removal by chelation indicates that manganese does not form strong interactions with the pulp[18,22,127]. A recent study examining the retention of added manganese by pulp has

reported that the weak interaction between the metal and the pulp is likely to involve the lignin component, as a minimal amount of manganese was retained when added to cellulose[147].

Figure 3.10 shows the solubility behaviour of the naturally occurring manganese present in *P. radiata* TMP at 50°C and pH 11.0. In the absence of peroxide and additives, very little of the manganese was found to exist in a soluble form. In contrast, a significant proportion of the manganese was found to be solubilized in the presence of hydrogen peroxide. As was observed for freshly prepared samples of manganese in section 3.5, the degree of solubilization was dependent on the concentration of peroxide present. This is clearly demonstrated by the substantial increase in the level of soluble manganese following the addition of a second peroxide charge after ~155 minutes, as shown in Figure 3.10.

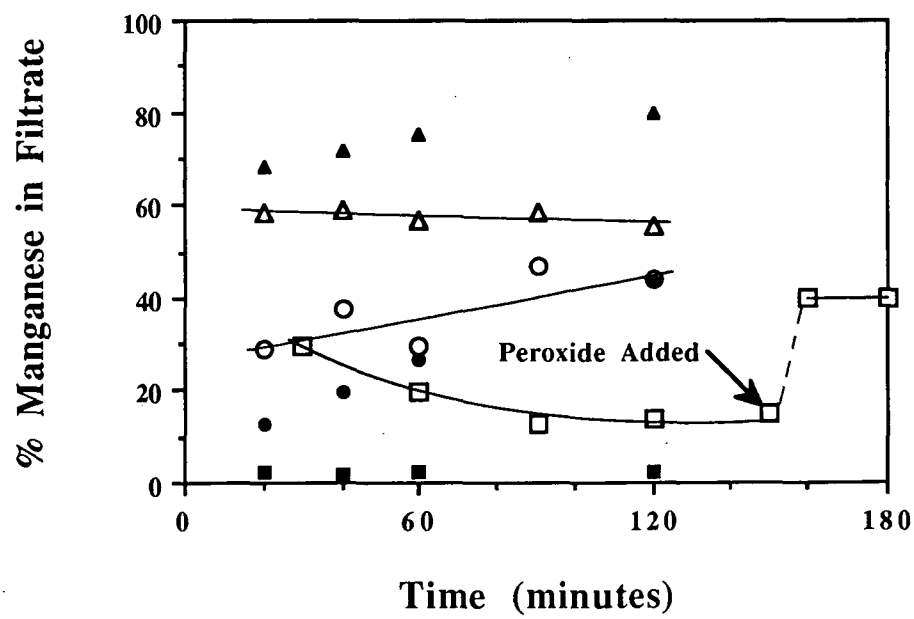

Figure 3.10 : Solubility of naturally the occurring manganese from TMP. (50°C, pH 11.0, 4% consistency ; open symbols : initial $[H_2O_2]$ = 0.035M, filled symbols : no H_2O_2 ; □ : Mn alone, Δ : Mn+Si, O : Mn+Mg).

Figure 3.10 also shows the effects of the addition of sodium silicate and magnesium on the solubility of the naturally occurring manganese. The presence of silicate clearly resulted in a significantly increased level of solubilization of the manganese, whereas the addition of magnesium had a much lower solubilizing effect. It is also apparent from Figure 3.10 that the presence of peroxide had little influence on the solubility behaviour of the naturally occurring manganese in the presence of additives.

The aging of manganese under conditions designed to simulate the refining process used for the production of TMP has previously been reported to have little or no effect on the metal species present[25]. It is not surprising then that a comparison reveals that the solubility behaviour of the naturally occurring manganese present in TMP is almost identical to that observed earlier for freshly prepared manganese in the presence of chelated TMP (see section 3.5).

3.7 Summary and Conclusions

The results obtained in the present study have demonstrated that the presence of the additives sodium silicate and magnesium can have a significant effect on the solubility of freshly prepared samples of transition metals in alkaline hydrogen peroxide solutions in the absence of pulp. In the presence of silicate, which was found to exist in a soluble form, the transition metals iron, copper and manganese were found to be present predominantly in a soluble form, suggesting that an interaction occurs between the silicate and the metal ions. This was highlighted in the case of copper which existed entirely in an insoluble form in the absence of silicate, but was predominantly soluble in the presence of silicate. The addition of magnesium was observed to have the opposite effect to that found for silicate. The transition metals were found to exist solely in an insoluble form in the presence of magnesium, which itself was insoluble. Again, the solubility behaviour indicates that a direct interaction of magnesium with the

transition metals must occur. The formation of the insoluble magnesium-metal species is likely to occur through either coprecipitation, or the absorption of the metals on precipitated magnesium hydroxide. The solubility behaviour exhibited for iron, copper and manganese in the presence of either sodium silicate or magnesium provides strong evidence supporting the concept of mixed metal complex formation, which has previously been proposed to account for the effects of additives on the transition metal catalysed decomposition of hydrogen peroxide (see section 2.6).

The presence of pulp was found to have a considerable influence on the solubility behaviour of freshly prepared samples of the transition metals, either alone or in the presence of magnesium. In the presence of magnesium, significant proportions of the transition metals were found to be in a soluble form, with the level of the soluble metal species increasing over the course of the reaction. Similar solubility behaviour was observed for magnesium itself. The increase in solubility was observed both in the presence and absence of peroxide, suggesting that soluble by-products of the reaction of peroxide and/or alkali with the pulp are involved in interactions with the metal species and magnesium. A similar mechanism appears to operate in the systems containing iron or copper in the absence of additives, as similar solubility behaviour to that found in the presence of magnesium was observed. In contrast, the solubility behaviour of manganese in the absence of additives was found to be dependent on the level of peroxide present.

The solubility of freshly prepared iron and manganese in the presence of sodium silicate was not found to be greatly affected by the inclusion of pulp. It appears that these metals form soluble silicate species in preference to interacting with the pulp. However, the solubility of added copper in the presence of silicate was found to be significantly lower in the presence of pulp, suggesting that the pulp may compete with silicate to form copper complexes.

A study of the naturally occurring iron and manganese present in *P. radiata* TMP revealed that their solubility behaviour, both in the presence and absence of sodium silicate and magnesium, closely resembled that observed for the added samples of freshly prepared metals. While manganese is expected to exist in a similar form in both cases[25], the resistance of the naturally occurring iron to removal by chelation indicated that it is not satisfactorily represented by the freshly prepared iron, which was found to be readily removed by chelation. In addition, aged iron, which has previously been used to represent the naturally occurring iron in mechanical pulp[22], is reported not to be solubilized by the addition of sodium silicate[25], and therefore does not adequately represent the naturally occurring iron species which was found to be solubilized in the presence of silicate. It appears that while the naturally occurring iron present in TMP exhibits some characteristics consistent with both aged and fresh iron, it is not satisfactorily represented by the addition of either form of the iron.

The solubility behaviour of the naturally occurring copper in the TMP could not be studied, as the metal was not present in a sufficiently high concentration.

The variations in the solubility behaviour of the transition metals, either in the presence or absence of additives, on the inclusion of pulp suggests that the form of the metals may be modified, presumably through interactions involving various components present in the pulp system. The possibility exists then that the catalytic behaviour of the transition metals towards peroxide decomposition may be modified in the presence of pulp. In addition, the response to additives such as sodium silicate or magnesium may also be modified. In order to determine the effects of the presence of pulp on the metal catalysed decomposition of peroxide a series of experiments has been conducted investigating effects of added transition metals and additives on peroxide decomposition in the presence and absence of chelated *P. radiata* TMP.

CHAPTER 4

Metal Catalysed Peroxide Decomposition Under Bleaching Conditions

4.1 Introduction

Despite the large volume of work concentrating on the effects of transition metal ions and additives during peroxide decomposition in the absence of pulp[24-27], much less is known about the mechanistic effects for the corresponding systems in the presence of pulp. The inclusion of pulp produces a much more complex system, and it is conceivable that the mechanism by which the transition metals operate, as well as the response to additives, could be significantly modified or indeed entirely different[24]. As metal catalysed peroxide decomposition reportedly leads to lower bleaching efficiency[18-23], it is desirable to develop a greater understanding of the reactions involved, together with the effects of additives which are commonly used as stabilizers.

The majority of evidence for the negative effects of transition metal ions during bleaching has been based on improved brightness gains and increased peroxide residuals following their removal or deactivation[9,18,23]. A number of studies of this type have identified manganese as the principle decomposition catalyst present as it is the most abundant and most readily removed by chelation[9,18,22,106]. In contrast, iron and copper have been found to be removed only to a minor extent by chelation, leading to the conclusion that they are inactive towards peroxide decomposition[9,18,22].

The addition of transition metal ions to pulp samples prior to bleaching provides an alternative method of studying their effects. This method has the advantage of enabling the effects of the individual metal ions to be studied in isolation. However, to date there have been few studies reported utilizing this technique and these have been of limited scope[19-22,96,146,147]. An early study by Reichert found that the addition of 5ppm of iron, copper or manganese resulted in appreciable increases in the rate of peroxide decomposition during bleaching[19]. Later studies by Read et al.[20] and Kutney

and Evans[96] reported the effects of added metal ions on peroxide decomposition in the presence of unbleached and prebleached pulps respectively. These studies confirmed that manganese was the most active decomposition catalyst in the presence of pulp, while iron and copper were found to be less effective[20,96]. A recent study by Colodette and Dence on the effects of the addition of aged iron and copper to α-cellulose derived from a Norway spruce TMP confirmed that strongly bound iron and copper are not catalysts for peroxide decomposition[22].

The effects of additives such as sodium silicate or magnesium on peroxide decomposition in the absence of pulp have been studied extensively, with particular combinations of metals and additives found to behave in different ways[21,24-27]. However, in the presence of pulp the study of these additives has concentrated on the optimization of reaction conditions to produce maximum bleaching efficiency. The major role attributed to silicate during bleaching has been the control of metal catalysed peroxide decomposition and yet there has been no detailed study on the effects of silicate on individual transition metals in the presence of pulp. Magnesium on the other hand has been found to be ineffective when used as the sole stabilizer during bleaching[28,31], despite the fact that it results in the modification of metal catalysed peroxide decomposition behaviour in the absence of pulp[24,26,27].

The present investigation has examined the effects of the transition metals iron, copper and manganese on peroxide decomposition, both in the presence and absence of pulp, together with the effects of the additives sodium silicate and magnesium. Computer modelling of peroxide consumption during bleaching reactions using chelated *P. radiata* TMP in the presence of added metals and additives enables the total consumption to be separated into two components; peroxide consumed by reactions with the pulp, and peroxide consumed by metal catalysed decomposition reactions. The rate of peroxide decomposition in the presence of pulp can then be compared

directly with the rate observed for the analogous reactions in the absence of pulp. These comparisons are facilitated by the use of constant pH conditions in both cases.

4.2 Use of Constant pH Conditions

Alkalinity is an extremely important parameter in the peroxide bleaching of mechanical pulps[23,139]. The primary role of the alkali is to generate the perhydroxyl anion, which is generally thought to be the active bleaching species[12,13,15,139], as shown in equation 4.1.

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H_2O \qquad \text{Eq. 4.1}$$

Clearly a high pH is favourable to promote the formation of this species[15,139]. However, high levels of hydroxide ions also promote chromophore creation reactions, ie. alkali darkening[12,23,133,139-142]. In addition, the rates of peroxide decomposition catalysed by various transition metal ions have been shown to be strongly dependent on the pH, with higher pH levels favouring rapid decomposition[15,21,23,136,137,139]. Under typical industrial conditions the influence of pH on the chemistry of bleaching systems is further complicated by the pH changing over the course of the reaction[137,139]. Generally a drop in pH is observed, attributable to the formation of acidic groups as a result of bleaching reactions, and the consumption of alkali in darkening reactions[137,139]. However, this is partially balanced by the catalytic decomposition of hydrogen peroxide which effectively raises the pH[27]. Consequently the degree of decomposition will have an effect on the extent to which the pH changes. Indeed, it has been reported that under certain conditions the pH initially increases due to base production from the decomposition of peroxide[162]. Clearly much of the chemistry of peroxide bleaching is fundamentally linked to the alkalinity of the system, the profile of which is defined by a number of interrelated chemical processes.

The use of constant reagent conditions enables the chemistry of the bleaching systems to be greatly simplified, allowing meaningful conclusions about reaction mechanisms to be obtained[133,221]. Constant pH conditions provide an excellent basis for the study of the effects of stabilizers on peroxide decomposition during bleaching. In the absence of controlled conditions the addition of stabilizers may influence the pH profile during the bleaching process either directly, due to the acidic or basic nature of the stabilizer, or indirectly, by altering the rate of peroxide decomposition, leading to results which may not reflect the true stabilizing ability of the additive[30].

In the present study the pH has been maintained at 11.0 by the addition of sodium hydroxide or sulphuric acid as required. The control of pH over the course of the bleaching reactions was facilitated by the use of low pulp consistency (4%). The use of identical conditions of constant pH for peroxide decomposition experiments in the absence of pulp allows for direct and meaningful comparisons to be made between the systems, and enables the effects of the presence of pulp to be determined. A reaction temperature of 50°C was used in all cases.

4.3 Determination of Peroxide Decomposition Rates

While the rate of peroxide decomposition can be measured directly in the absence of pulp, the addition of pulp to the system introduces a number of competing reactions which also lead to the consumption of peroxide[31]. Bleaching, non-bleaching and darkening reactions are all reported to take place during peroxide bleaching together with metal catalysed decomposition reactions[31]. As a result, simple measurements of peroxide residuals during bleaching only provide information about the total level of peroxide consumption and do not provide any indication of the relative levels of peroxide consumed in the individual component reactions.

The measurement of oxygen evolution during bleaching has been used by a number of

workers to determine the level of peroxide decomposition during bleaching[21,137]. This method relies on the quantitative conversion of hydrogen peroxide to oxygen as a result of metal catalysed decomposition reactions. However, the consumption of oxygen during the bleaching period introduces an error into the measurement of the rate of oxygen evolution and therefore the calculated rate of peroxide decomposition[137]. In addition, reactive decomposition products of hydrogen peroxide such as hydroxyl radicals may react with various components of the pulp[151-156] and thus will not be converted into oxygen, introducing a further source of error in the calculation of the decomposition rate. The measurement of oxygen evolution may therefore be expected to give a conservative estimate of the level of peroxide decomposition during bleaching.

The mathematical modelling of peroxide consumption during bleaching provides an alternative method of calculating the relative rates of catalytic peroxide decomposition and peroxide consumption in reactions with pulp during bleaching. This method is based on the assumption that the rates of peroxide consumption through these two processes can be considered to be independent and additive. Using mathematical models based on appropriate kinetic expressions it is then possible to calculate the rates of the individual reactions contributing to the total peroxide consumption during bleaching.

4.3.1 Mathematical Models for Peroxide Consumption during Bleaching

Total peroxide consumption during pulp bleaching can be represented by the sum of two components:

$$\frac{-d[H_2O_2]}{dt} = \frac{-d[H_2O_2]_p}{dt} + \frac{-d[H_2O_2]_m}{dt} \qquad \text{Eq. 4.2}$$

where $[H_2O_2]_p$ is the peroxide consumed by the pulp and $[H_2O_2]_m$ represents peroxide decomposed in side reactions due to the presence of metal ions. Numerous studies have shown that, in the presence of pulp[137] and in the absence of pulp[27,168], catalytic decomposition of peroxide can be represented by a first-order kinetic expression of the type:

$$\frac{-d[H_2O_2]_m}{dt} = k_m[H_2O_2] \qquad \text{Eq. 4.3}$$

This relationship can be used in equation 4.2 to represent a set of parallel first-order decomposition processes, with overall rate constant k_m. Various approaches can be taken to formulating an expression to represent peroxide consumption due to bleaching processes:

Model A

A study of peroxide consumption using a groundwood pulp has been reported by Martin[137]. The rate of peroxide decomposition, measured by oxygen evolution, was found to be first-order[137]. Total peroxide consumption, followed by a titrimetric procedure was also shown to be first-order, implying that peroxide consumption through bleaching reactions also follows first-order kinetics[137]:

$$\frac{-d[H_2O_2]_p}{dt} = k_p[H_2O_2] \qquad \text{Eq. 4.4}$$

Model B

An empirical kinetic expression of the form:

$$\frac{-d[Chr]}{dt} = k[H_2O_2]^a[OH^-]^b[Chr]^c \qquad \text{Eq. 4.5}$$

has been used by several workers to describe peroxide bleaching kinetics[133,144,222], where [Chr] represents the concentration of chromophores. In all cases reported, the exponent (c) requires a high numerical value (usually in the range 4-5) to provide an adequate fit with experimental data[133,144,222]. Assuming conditions of constant pH ($[OH^-]$ constant) a relationship describing peroxide consumption can be postulated according to the expression:

$$\frac{-d[H_2O_2]_p}{dt} = k_p[H_2O_2]^n \qquad \text{Eq. 4.6}$$

where a high order in peroxide (n) would also be expected. It should be noted that model A is a special case of model B, with n=1.

4.3.2 Application of the Proposed Mathematical Models

Application of the proposed models for peroxide consumption assumes that the rates of peroxide consumption through bleaching processes and catalytic decomposition induced by metal ions can be regarded as independent and additive. In order to examine the influence of metal ions on peroxide decomposition in the presence of pulp it is necessary to establish a baseline experimental condition where the effects of metal ions in the system are minimised. In this study, this was taken as a bleaching system containing sodium silicate with a chelated pulp. Under these conditions maximum stabilization of the peroxide was obtained. It should be noted that the addition of magnesium produced similar levels of peroxide stability. However, the addition of magnesium also resulted in decreased brightness gains under certain conditions, implying that it may interfere with the bleaching reactions (see sections 5.6.1 and 5.6.2). A recent study has demonstrated that sodium silicate is not beneficial in the near absence of transition metal ions, implying that the sole role of silicate is the deactivation of these metals[139].

Experiments conducted under constant conditions of pH and peroxide concentration show that introduction of silicate, or removal of metal ions from the pulp by chelation and washing has a negligible effect on brightness gain, Figure 4.1. This implies that the dominant influences of added silicate or transition metals are on peroxide decomposition, rather than through other processes directly involving chromophore removal or formation. This is also illustrated in Figure 4.2 which shows that addition of iron, copper or manganese to a chelated pulp had little influence on brightness response with constant reagent concentrations. These results suggest that under alkaline conditions, bleaching pathways which might strongly depend on the concentration of peroxide decomposition products (eg radical species) do not exert a major influence on the rate of chromophore removal or formation. This is consistent with the findings of a recent study by Hobbs and Abbot investigating the role of hydroxyl radicals during peroxide bleaching processes[90].

Figures 4.3 and 4.4 show results for model fitting corresponding to peroxide consumption during bleaching of chelated TMP in the presence and absence of sodium silicate respectively. It is apparent that model B provides a better representation of the experimental behaviour than model A, suggesting that the peroxide consumption behaviour during bleaching cannot simply be related to first-order kinetics. Using the calculated values of the parameters k_p for model A and k_p and n for model B corresponding to maximum stabilization, it is then possible to calculate values of the rate constant (k_m) to account for excess peroxide decomposition in subsequent bleaching experiments.

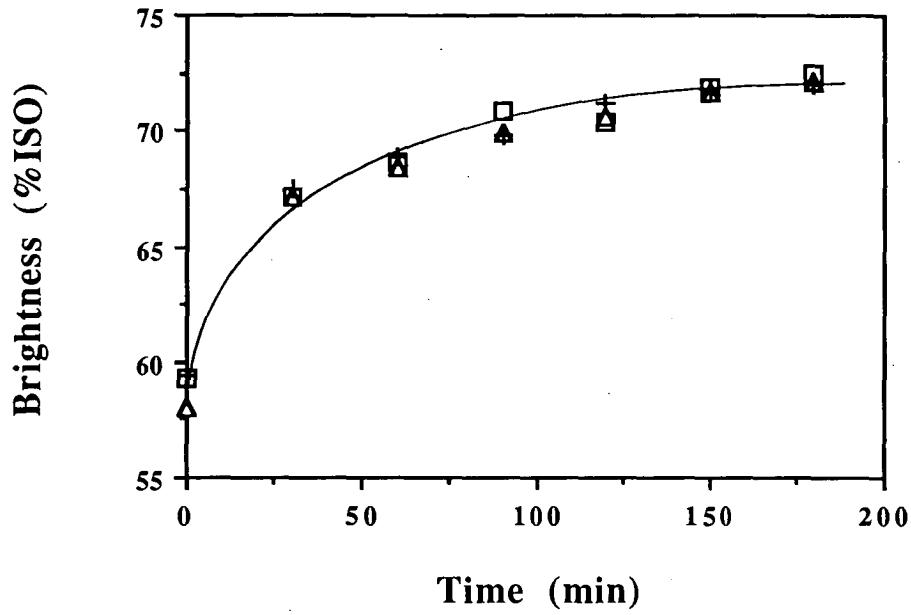

Figure 4.1 : Effects of chelation or silicate addition on the bleaching of TMP under constant conditions. (50°C, pH 11.0, 4% consistency, $[H_2O_2]$=0.035M, [silicate] = 3.46×10^{-2} M; □ : TMP, Δ : TMP+silicate, + : chelated TMP).

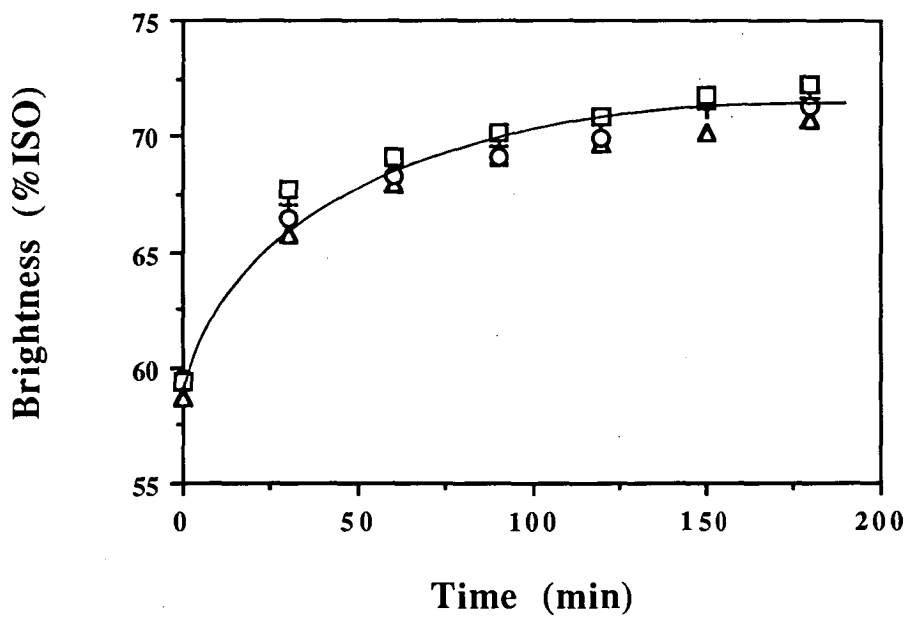

Figure 4.2 : Effects of added metal ions on the bleaching of chelated TMP under constant conditions. (50°C, pH 11.0, 4% consistency, $[H_2O_2]$=0.035 M; + : no added metals, Δ : [Fe] = 8.92×10^{-6} M, O : [Cu] = 6.36×10^{-5} M , □ : [Mn] =3.66×10^{-5} M).

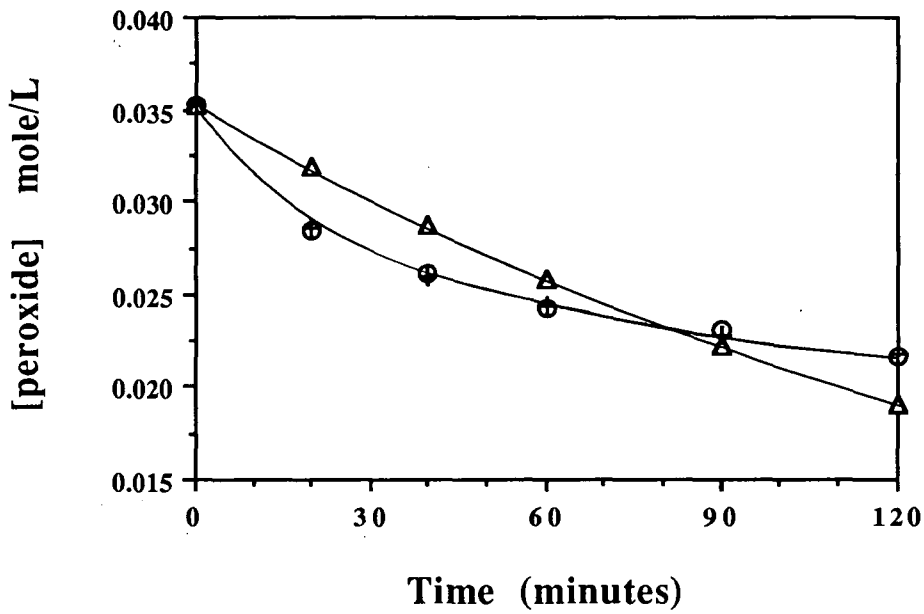

Figure 4.3 : Computer model fittings for peroxide consumption during the bleaching of chelated TMP in the presence of 3.32×10^{-2} M sodium silicate. (O : experimental , Δ : Model A , + : Model B).

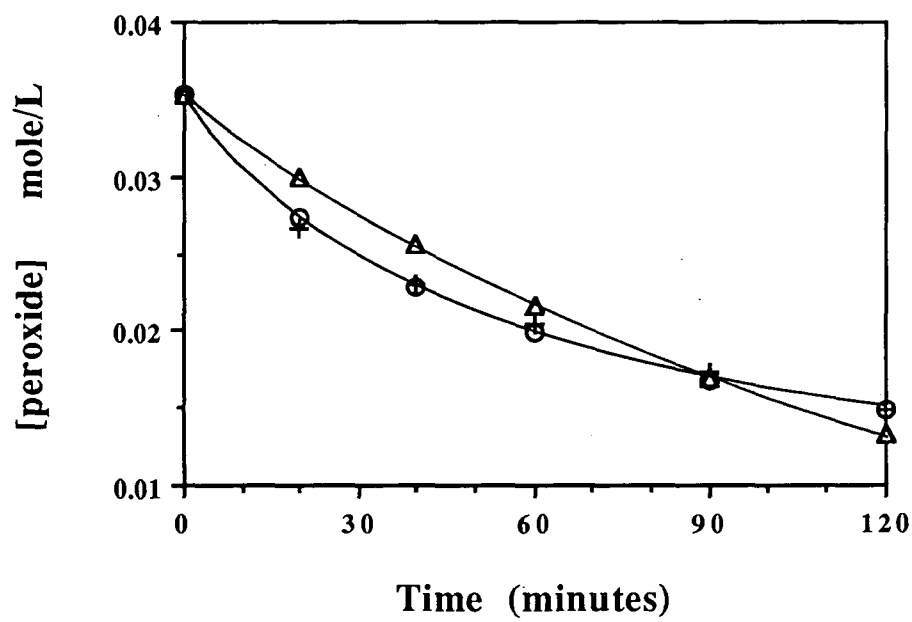

Figure 4.4 : Computer model fittings for peroxide consumption during the bleaching of chelated TMP. (O : experimental , Δ : Model A , + : Model B).

4.4 Peroxide Decomposition in the Absence of Added Transition Metal Ions

The use of stabilizing agents to control the decomposition observed in the absence of added metal ions is clearly not feasible in a study of this type, as they could interfere with the behaviour observed in subsequent experiments examining the effects of the added metal ions. As a result a degree of peroxide decomposition is observed in the absence of added metal ions.

Figure 4.5 shows that the decomposition observed in the absence of pulp is almost completely retarded by the addition of DTPA, implying that the reaction is induced by transition metal impurities. The peroxide decomposition in the presence of pulp can be reduced by the removal of metal ions by chelation and washing. However, the pre-chelation of the pulp does not completely eliminate the metal-catalysed reactions, as evidenced by the decreased peroxide consumption observed on the addition of sodium silicate, as shown in Figure 4.6. It has recently been reported that it is possible with a more exhaustive "superchelation" process to reduce peroxide decomposition to such a low level that the addition of silicate does not result in further stabilization[139]. It can be concluded that the peroxide decomposition observed during the bleaching of the regularly chelated pulp used in this study was due to residual metal ions.

4.4.1 Effects of Sodium Silicate in the Absence of Added Metal Ions

The effects of sodium silicate on the calculated first-order rate constants for peroxide decomposition in the absence of added metal ions are shown in Figure 4.7. The addition of increasing levels of silicate was found to have a similar effect on the peroxide decomposition in the presence and absence of pulp, Figure 4.7. While high levels of silicate addition resulted in the almost complete stabilization of peroxide, the

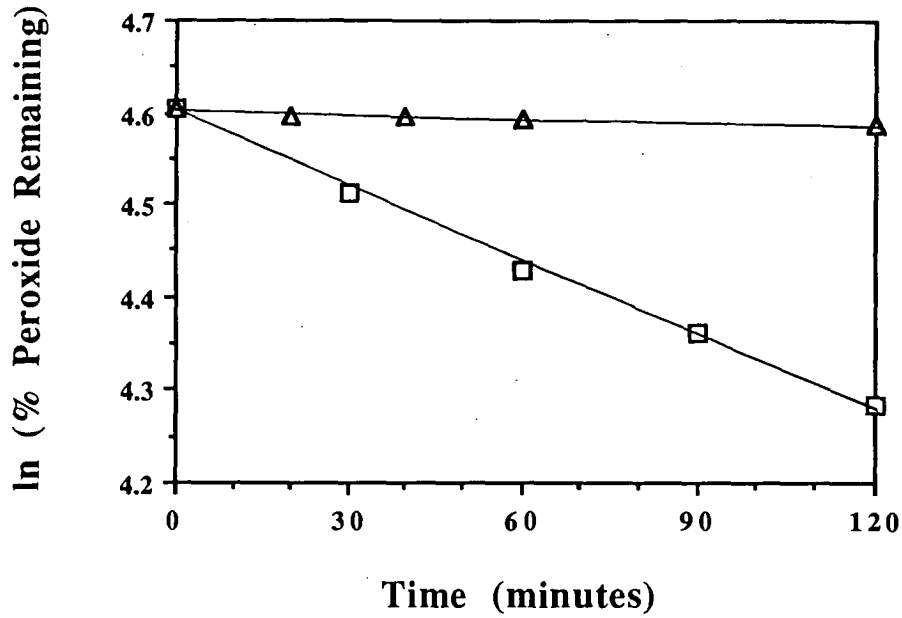

Figure 4.5 : First-order plots for peroxide decomposition in the presence (Δ) and absence (□) of 5.28×10^{-5} M DTPA. (50°C, pH 11.0, initial $[H_2O_2] = 0.035M$).

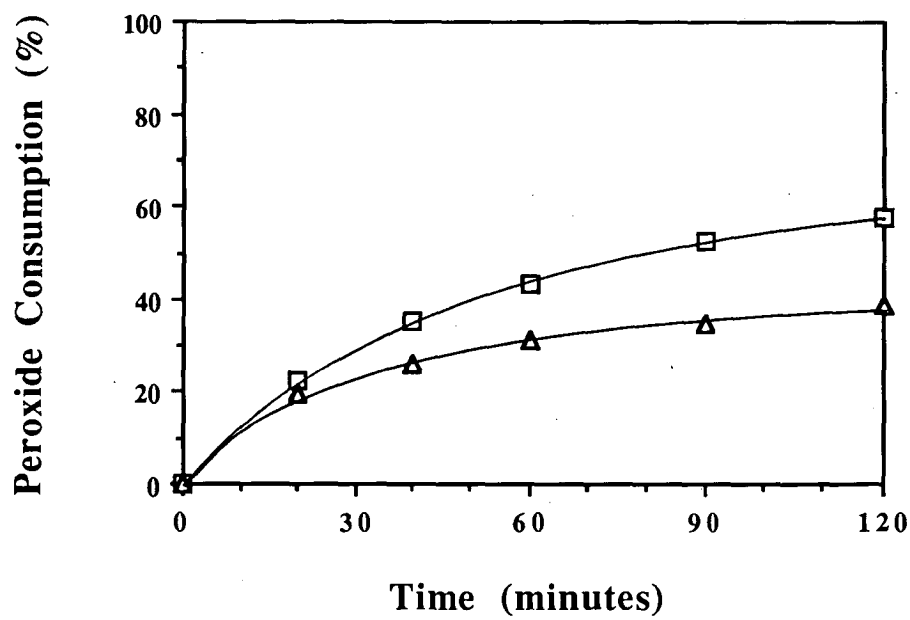

Figure 4.6 : Peroxide consumption during the bleaching of chelated TMP in the presence (Δ) and absence (□) of 3.3×10^{-2} M sodium silicate. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2] = 0.035M$).

addition of lower levels led to increased rates of metal-catalysed decomposition.

Accelerated rates of peroxide decomposition in the presence of silicate have been reported previously[24,25] with the trace metals present suggested to have a significant influence on the effects in the presence of silicate[24]. The peroxide decomposition observed in the present study can be attributed to metal ion impurities. Silicate has previously been shown to influence the catalytic activity of transition metal ions by the formation of mixed complexes (see section 2.6). It seems likely that the observed effects in the absence of added metal ions are due to the interaction of silicate with certain metal ion impurities present in the respective systems in the presence and absence of pulp.

4.4.2 Effects of Magnesium in the Absence of Added Metal Ions

Figure 4.8 shows the effects of magnesium nitrate addition on the calculated first-order rate constants for peroxide decomposition in the absence of added metal ions. The results obtained in the absence of pulp are consistent with the findings of other workers that small doses of magnesium are capable of almost completely stabilizing alkaline solutions of hydrogen peroxide[4,26,28]. Figure 4.8 also shows that the addition of magnesium reduced the level of peroxide decomposition in the presence of pulp. This behaviour was unexpected as magnesium has previously been found to be ineffective as a stabilizer during bleaching in the absence of silicate[28,30,31]. However, recent studies have reported that the addition of magnesium can be beneficial during bleaching, provided high doses are employed[167]. The effects of magnesium as the sole stabilizing agent during bleaching are discussed in more detail in section 5.6.

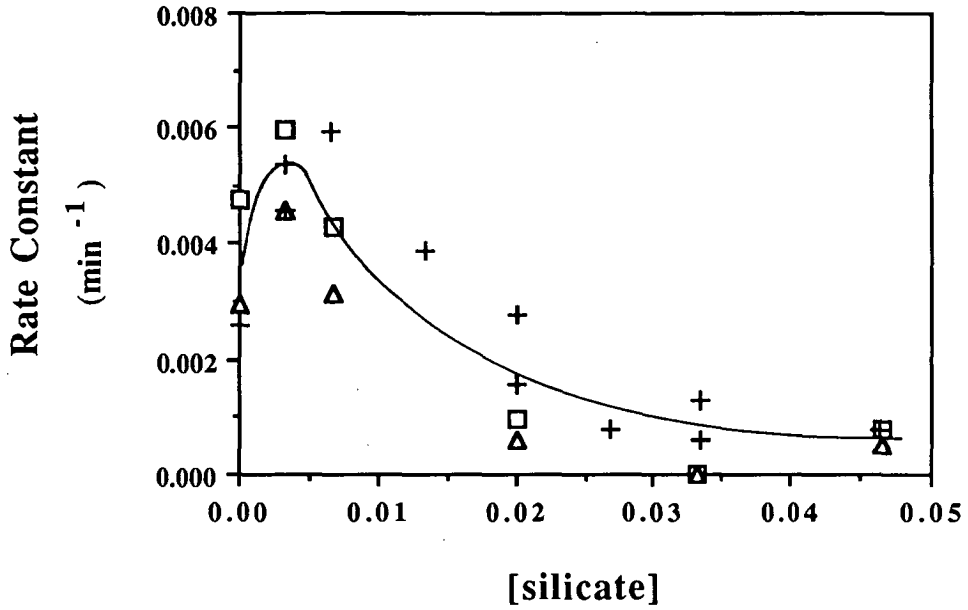

Figure 4.7 : Effects of silicate addition on the rates of peroxide decomposition in the presence and absence of chelated TMP. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2] = 0.035M$; + : no pulp, Models - Δ : A , □ : B).

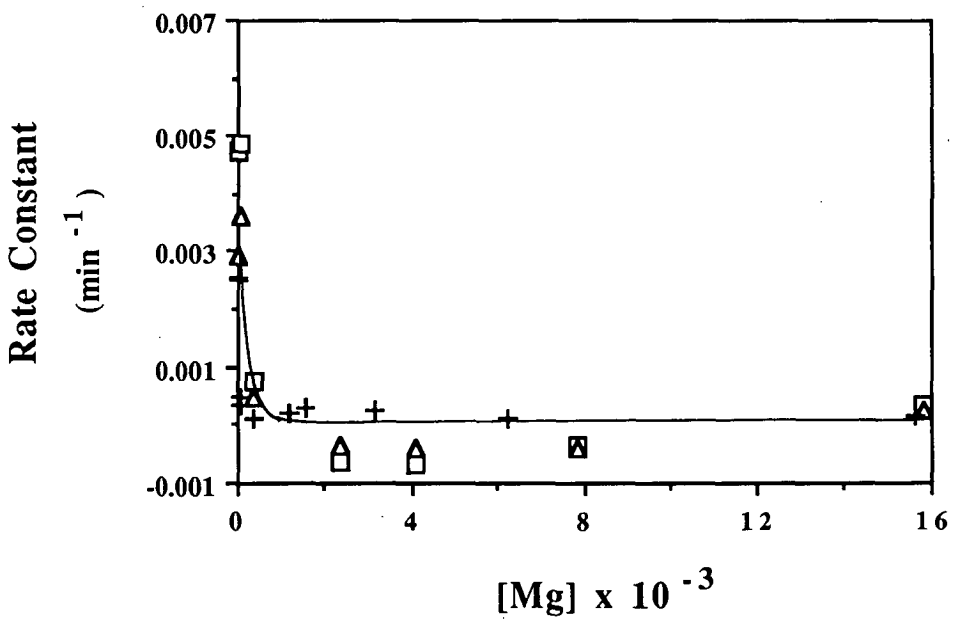

Figure 4.8 : Effects of magnesium addition on the rates of peroxide decomposition in the presence and absence of chelated TMP. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2] = 0.035M$; + : no pulp, Models - Δ : A , □ : B).

4.5 Peroxide Decomposition in the Presence of Added Iron

The iron catalysed decomposition of hydrogen peroxide in the absence of pulp has previously been shown to be closely related to the hydrolysis species present (see sections 2.3, 2.3.3.1). The catalytic species formed on the aging of iron prior to the addition of peroxide have been shown to be less active than the species initially present when fresh iron is used. The aging of iron has also been reported to influence its behaviour in the presence of pulp[127,182]. The binding of iron to cellulose has been shown to be closely related to the degree of hydrolysis, with aged iron binding tenaciously, while weaker bonds are formed when fresh iron is adsorbed[127,182]. The conditions which prevail in the manufacture of mechanical pulps favour the formation of aged iron species and as a result the majority of iron is tightly bound to the pulp[127]. It has recently been demonstrated that aged iron is not active towards the decomposition of hydrogen peroxide in the presence of pulp[22].

The effects of the addition of fresh and aged ferric nitrate on peroxide decomposition in the absence of pulp are shown in Figure 4.9. In both cases stabilization of peroxide was observed for low levels of addition, while higher levels of addition resulted in increased peroxide decomposition. This is clearly demonstrated in Figure 4.10 which shows the variation in first-order rate constants as the level of iron was increased.

The stabilization of alkaline hydrogen peroxide solutions by the addition of iron has been reported previously[24,53]. However, no satisfactory explanation has been given to explain this phenomena[53]. The peroxide decomposition in the absence of added iron has been shown to be induced by metal ion impurities. Stabilization under these conditions can therefore be expected to be due to the deactivation of these catalytic species. The formation of mixed hydrolysis species between iron and other metallic elements has been demonstrated previously, resulting in the modification of

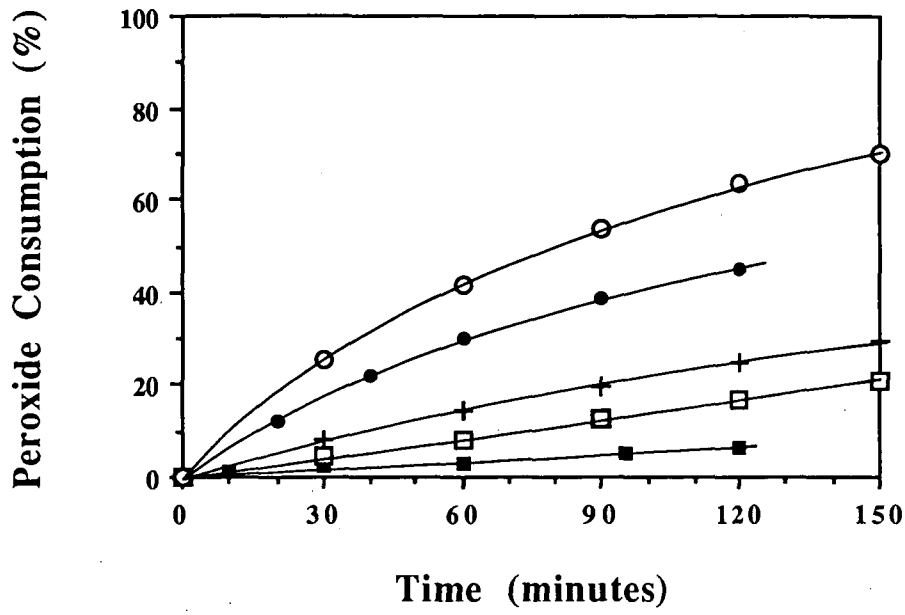

Figure 4.9 : Effects of the addition of iron on peroxide decomposition in the absence of pulp. (50°C, pH 11.0, initial $[H_2O_2]$ = 0.035M ; + : no Fe , Fresh Fe - □ : $3.6x10^{-5}$ M , ○ : $4.0x10^{-4}$ M ; Aged Fe - ■ : $3.6x10^{-5}$ M , ● : $3.6x10^{-4}$ M).

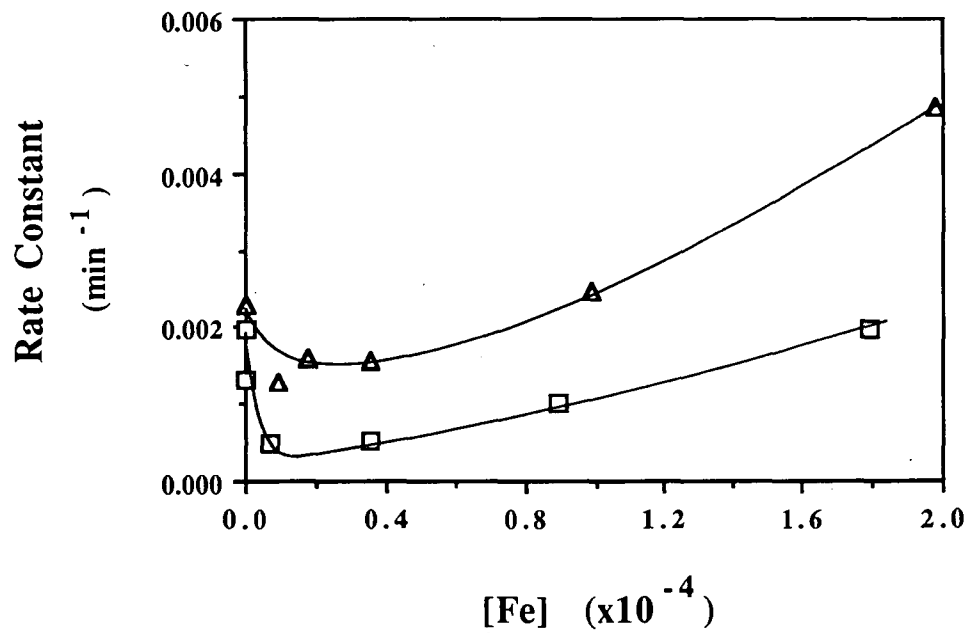

Figure 4.10 : Effects of the addition of fresh (□) and aged (△) iron on first-order rate constants for peroxide decomposition in the absence of pulp. (50°C, pH 11.0, initial $[H_2O_2]$ = 0.035M).

the catalytic activity of the iron (see section 2.6). Iron has also been reported to be an efficient collector for the coprecipitation of a wide range of metallic impurities[208-210]. It seems likely then that the catalytic activity of the trace metal impurities are reduced by their interaction with the added iron species. As a result, stabilization may be observed for certain levels of iron, where the rate of iron catalysed peroxide decomposition is less than that initially observed due to the metallic impurities. Figure 4.11 shows that the rate of decomposition is directly proportional to the concentration of iron added for both fresh and aged iron samples. This figure also clearly demonstrates the higher catalytic activity of fresh iron in comparison with that of the aged iron.

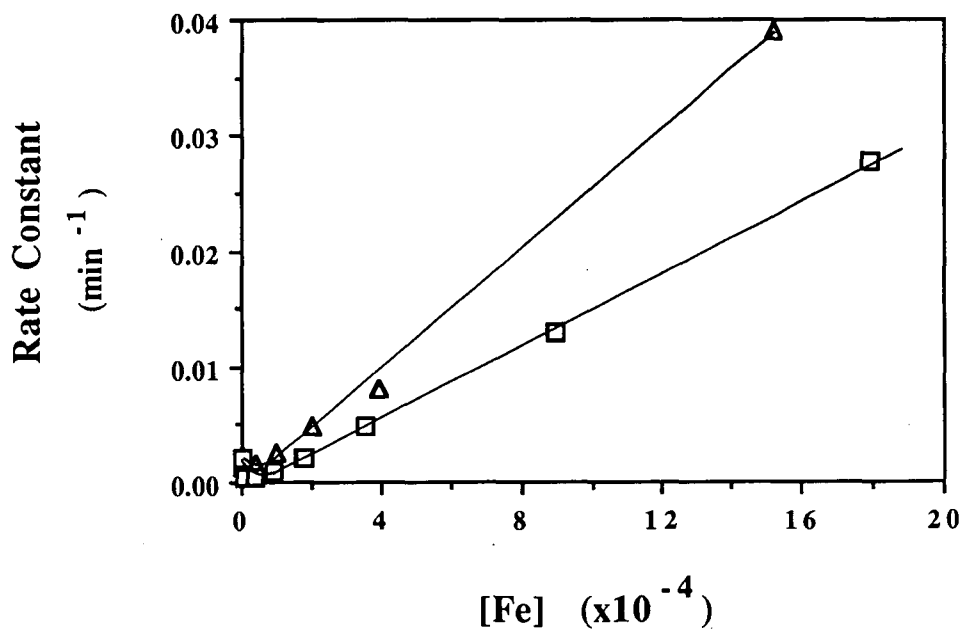

Figure 4.11 : Effects of the addition of fresh (□) and aged (△) iron on first-order rate constants for peroxide decomposition in the absence of pulp. (50°C, pH 11.0, initial $[H_2O_2]$ = 0.035M).

The effects of added iron on peroxide consumption in the presence of chelated TMP are shown in Figure 4.12. In these experiments, the level of iron introduced was 3.58×10^{-5} M, the equivalent of ~50ppm on pulp. The addition of aged iron was found

to have little effect on peroxide consumption in the presence of pulp. In contrast, the addition of fresh iron resulted in a considerable increase in peroxide consumption. This result was somewhat surprising as the addition of a similar level of fresh iron in the absence of pulp had little effect on peroxide decomposition. A comparison of the calculated first-order rate constants for peroxide decomposition induced by freshly prepared iron in the presence of pulp with the measured first-order rate constants in the absence of pulp is shown in Figure 4.13. Clearly the presence of pulp greatly enhanced the catalytic activity of the freshly prepared iron.

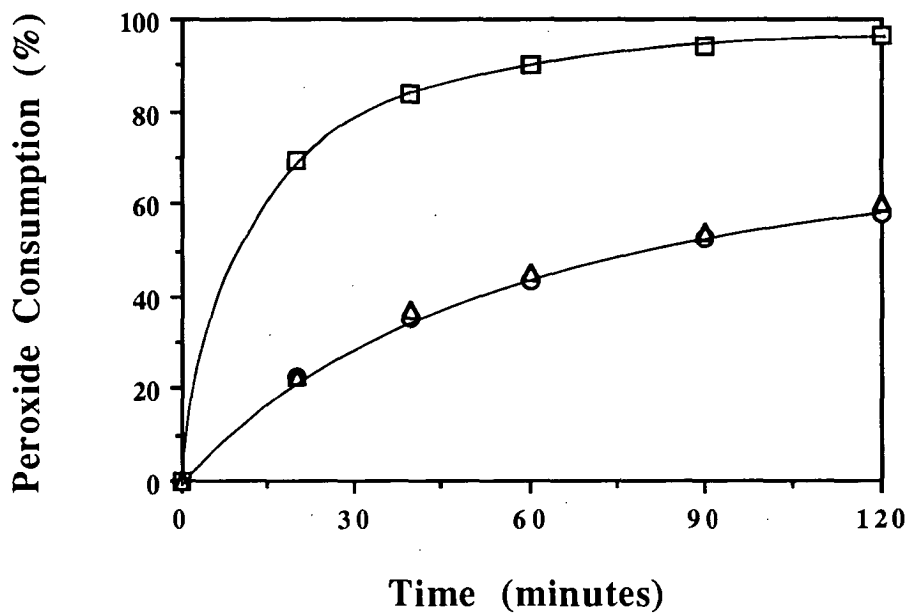

Figure 4.12 : Effects of the addition of fresh and aged iron on peroxide consumption during the bleaching of chelated TMP. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$ = 0.035M, [Fe] = 3.58×10^{-5} M ; O : No Fe , □ : fresh Fe , Δ : aged Fe).

A number of studies have previously reported the effects of the addition of iron on peroxide consumption in the presence of pulp[19-22,96]. Reichert reported that the addition of 5ppm of iron resulted in an appreciable increase in the rate of peroxide decomposition in the presence of pulp wood[19]. Studies by Kutney and Evans [96] and

by Burton and Campbell[21] investigating the effects of higher levels of iron addition also found that increased peroxide decomposition occurred. In contrast, a study by Read et al. observed that the addition of 5ppm of iron had little effect on peroxide consumption during bleaching[20], while Colodette and Dence reported that aged iron was not catalytically active in the presence of pulp[22]. These results indicate that iron can exist in at least two forms (one active and one inactive) in the presence of pulp. The results of the present study confirm that aged iron is inactive in the presence of pulp. However, in the presence of pulp the catalytic activity of fresh iron was greatly enhanced, suggesting that a new, highly active, catalytic species is formed.

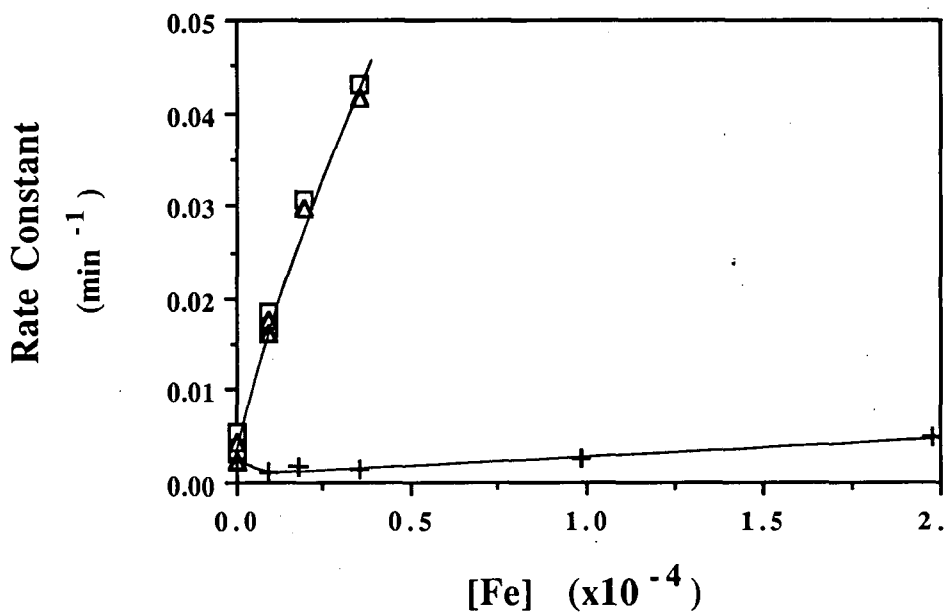

Figure 4.13 : Comparison of rates of iron catalysed peroxide decomposition in the presence and absence of chelated TMP. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2] = 0.035M$; + : no pulp, Models - Δ : A , □ : B).

Numerous studies have shown that the majority of iron present in mechanical pulps is tightly bound to the pulp and thus is not readily chelatable[9,18,22,127]. In this form, the iron reportedly presents no problem during bleaching as it is not catalytically

active[9,18,22]. However, the possibility exists that any potentially chelatable iron which is not removed may form highly catalytically active species resulting in increased peroxide decomposition and thus decreased bleaching efficiency. This danger was highlighted by a recent study which reported the formation of a catalytically active complex between iron and DTPA despite the use of an aged iron sample[26]. It has also been reported that metal ion impurities introduced with mill waters are likely to be in an active form[19] and therefore any iron introduced in this way may also present a problem during bleaching.

It has previously been demonstrated that the addition of pulp results in the modification of the solubility behaviour of iron, suggesting that a new species may be formed (see section 3.3). In order to investigate the nature of the highly active iron species which can form in the presence of pulp, a series of experiments have been conducted to determine the effects of individual pulp components on the catalytic activity of freshly prepared iron.

4.5.1 Iron Catalysed Peroxide Decomposition in the Presence of Bleached Kraft Pulp

The binding of iron to cellulose is well established and has been investigated in detail by a number of workers[127,182]. It has been demonstrated that cellulose can form either strong or weak bonds with iron depending on its form, with the aging of iron favouring the formation of strong interactions[127,182]. The possibility exists that the initial hydrolysis species present when fresh iron is added to pulp can interact with the cellulose component of the pulp resulting in the formation of a new catalytic species. In order to investigate this possibility a bleached *P. radiata* kraft pulp was used as a source of cellulose fibres[223].

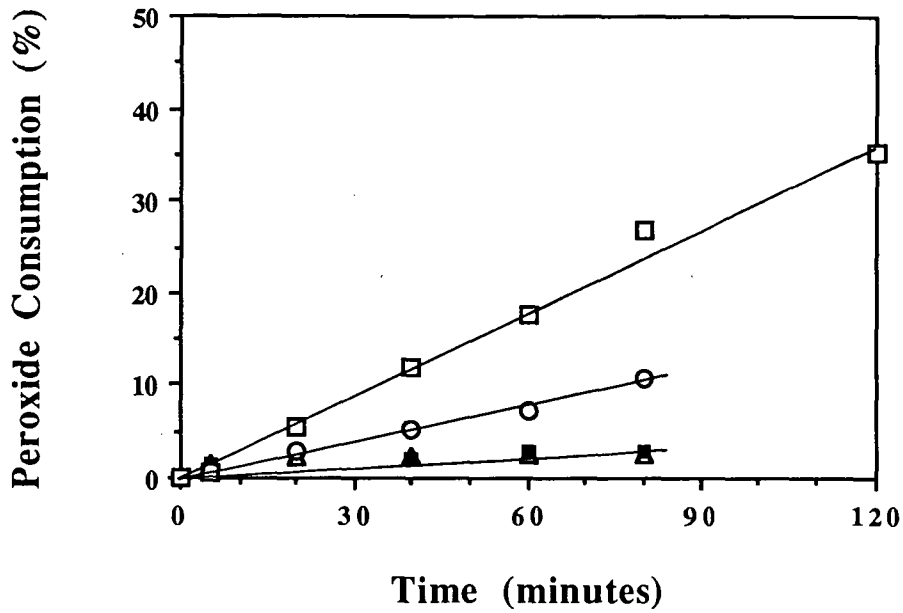

Figure 4.14 : Effects of fresh iron nitrate on peroxide consumption in the presence of bleached kraft pulp. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$ = 0.035M; Δ : No Fe, ■ : [Fe] = 8.92×10^{-6} M, O : [Fe] = 3.56×10^{-5} M, □ : [Fe] = 7.18×10^{-5} M).

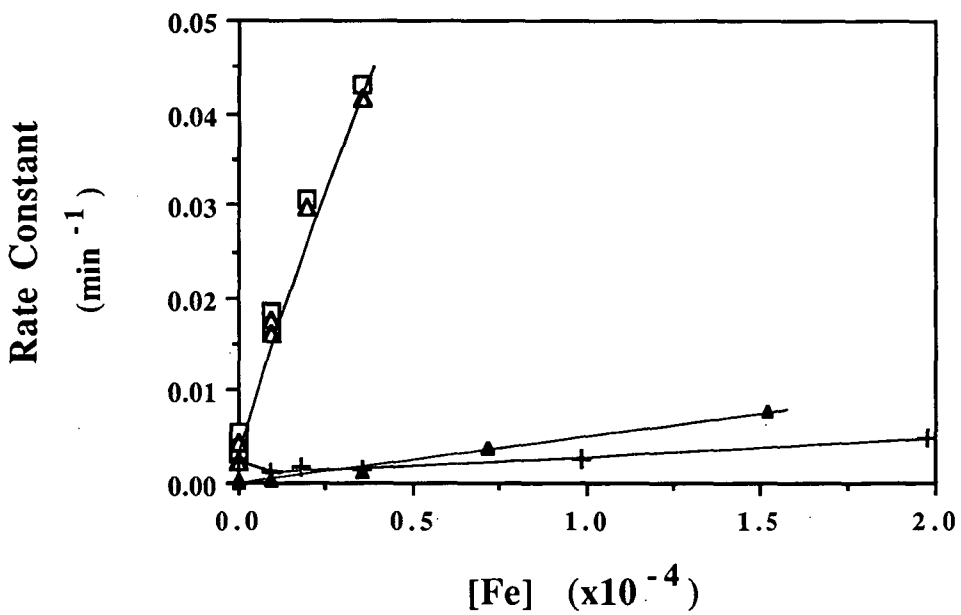

Figure 4.15 : Rates of iron catalysed peroxide decomposition in the presence of chelated TMP (Models - Δ : A , □ : B), bleached kraft pulp (▲), and in the absence of pulp (+). (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$ = 0.035M).

Figure 4.14 shows the effect of the addition of various levels of fresh iron on peroxide decomposition in the presence of kraft pulp. The presence of kraft pulp does not have a significant influence on the catalytic activity observed for iron, as shown in Figure 4.15. This result implies that the increased catalytic activity observed for fresh iron in the presence of *P. radiata* TMP is not due to interactions with the cellulose fibres.

4.5.2 Iron Catalysed Peroxide Decomposition in the Presence of Model Compounds

This study was designed to determine whether the presence of various model compounds, which are representative of components likely to be present during the bleaching of mechanical pulp, have any effect on the catalytic activity of freshly prepared iron. The presence of metal-organic complexes has previously been discussed in relation to peroxide decomposition during bleaching[18]. However, it is difficult to determine whether the complexed species or the free metal ions are the active catalytic agents during the bleaching of pulp[18]. Naturally occurring trace metals are reported to exist in the pulp as metal-organic complexes[11,18,20], with the catalytic activity depending on the stabilities of the natural chelates[18]. It seems feasible then that the complexation of added metal ions may result in the formation of new catalytic species.

Table 4.1 shows the effects of the addition of various aromatic lignin model compounds on peroxide consumption in the presence of fresh iron. The presence of compounds containing the basic C-9 structural unit of lignin, cinnamic acid and 3,4-dimethoxycinnamic acid, were not found to result in a significant increase in the catalytic activity of iron. Similarly, experiments conducted with aromatic model compounds containing a variety of functional groups did not reveal an increased propensity for the iron catalysed decomposition of peroxide. While the level of

peroxide consumption observed for iron in the presence of vanillin was considerably higher than that observed for the other lignin model compounds tested, the increased consumption can be attributed to the reaction of peroxide with vanillin.

Table 4.1 : Effects of Lignin Model Compounds on the Iron Catalysed Decomposition of Hydrogen Peroxide. (50°C, pH 11.0, initial $[H_2O_2]$ = 0.035M, [Fe] =3.6×10^{-5} M, [Model Compounds] = 3.6×10^{-3} M, 60 minutes reaction time).

Model Compounds	Peroxide Consumption (%) Model Compound+ Fe	Peroxide Consumption (%) Model Compound Alone
No Model	17.0	-
Cinnamic Acid	25.4	6.7
3,4-Dimethoxycinnamic acid	24.6	7.8
4-Hydroxy-3-Methoxybenzoic Acid	22.3	8.9
3,4-Dimethoxybenzoic Acid	20.6	12.3
3,4,5-Trimethoxyacetophenone	27.0	12.2
Acetovanillone	27.9	13.8
Vanillin	63.9	54.7

The structure of lignin is extremely complex[224] and may be expected to give rise to an extensive range of organic compounds containing a wide range of functional groups. While the complexity of the system precludes a detailed study of all the compounds present, the present study gives no indication that organic compounds derived from the lignin are responsible for the increased catalytic activity observed for fresh iron in the presence of *P. radiata* TMP.

The presence of hydroxy-acids or other soluble products of oxygen bleaching have been reported by Gilbert et al. to play a major role in facilitating the metal catalysed decomposition of peroxide[115]. The formation of carboxylic acids as products of peroxide bleaching is well known, reportedly originating from reactions between hydrogen peroxide and lignin and also from the deacetylation of hemicelluloses[225,226]. Table 4.2 shows the effects of the addition of glucuronic, gluconic and adipic acids on the iron catalysed decomposition of peroxide. Clearly the presence of gluconic acid resulted in a dramatic increase in the consumption of peroxide, while the addition of glucuronic acid also appeared to increase the peroxide consumption, but to a much lesser extent. In contrast, the addition of adipic acid had little effect on the rate of peroxide consumption in the presence of iron. The catalytic activity of iron in the presence of gluconic acid has been reported previously[115]. The gluconic acid was reported to maintain the homogeneity of the system through the formation of a soluble complex with iron[115].

Low molecular weight carboxylic acids are commonly present in spent peroxide bleaching liquors due to reactions of peroxide with various lignin components[225,226]. Table 4.2 also shows the consumption of peroxide in iron catalysed decomposition reactions in the presence of oxalic, acetic and formic acids. While the addition of acetic and formic acid had little effect on the decomposition of peroxide, the addition of oxalic acid appreciably enhanced the catalytic activity of iron. As with gluconic acid, it

seems likely that the formation of a complex between the iron and oxalic acid may result in a more active catalytic species. Indeed, oxalic acid has previously been reported to be an effective chelant for the removal of naturally occurring iron from TMP[127].

Table 4.2 : Effects of Carboxylic Acids on the Iron Catalysed Decomposition of Hydrogen Peroxide. (50°C, pH 11.0, initial $[H_2O_2]$ = 0.035M, [Fe] =$3.6x10^{-5}$ M, [Model Compounds] = $3.6x10^{-3}$ M, 60 minutes reaction time).

Model Compounds	Peroxide Consumption (%) Model Compound+ Fe	Peroxide Consumption (%) Model Compound Alone
No Model	17.0	-
Gluconic Acid	94.9*	7.1
Glucuronic Acid	57.7	35.5
Adipic Acid	27.9	9.1
Oxalic Acid	59.8	9.6
Acetic Acid	11.7	2.6
Formic Acid	17.3	4.6

* 20 minutes reaction time.

The concept of the formation of metal complexes leading to higher catalytic activity is not new[21,26,37,40,41,73,82,86,87]. The chelation of iron by DTPA has been reported by many workers to result in increased rates of peroxide decomposition[21,26]. A study of the solubility of freshly prepared iron showed that the majority of the iron was in an insoluble form in the presence of pulp, whereas under identical conditions in the absence of pulp the iron was found to be primarily in a soluble form, supporting the notion of pulp-iron interactions (see section 3.3). An increase in the solubility of iron over the course of the bleaching reaction may indicate that some iron becomes bound to soluble by-products of the reactions of peroxide or alkali with the pulp (see section 3.3). The present study has established that the catalytic activity of fresh iron is significantly increased in the presence of the model compounds gluconic acid and oxalic acid. These two compounds represent just two of a wide range of compounds containing carboxylic acid functionalities which are commonly present in peroxide bleaching systems[225,226]. It seems likely then that the increased rate of peroxide decomposition observed for fresh iron in the presence of *P. radiata* TMP is due to the formation of complex species between the iron and components of the pulp containing carboxylic acid functional groups. This is consistent with the results obtained on the addition of aged iron to the pulp, where little iron is available to form complexes of this type and hence no increase in catalytic activity is observed.

4.5.3 Effects of Sodium Silicate on Iron Catalysed Peroxide Decomposition

The effects of the addition of increasing levels of sodium silicate on the iron catalysed decomposition of peroxide in the presence and absence of pulp are reflected in the variation of the first-order rate constants, as shown in Figure 4.16. The large variation in rate constants corresponding to the systems in the absence of silicate reflects the differences in the catalytic activities of fresh iron in the presence and absence of pulp.

Comparison with Figure 4.7 reveals that the behaviour observed for the addition of silicate to iron, in the absence of pulp, closely resembles that obtained under identical conditions in the absence of added iron. The addition of low levels of silicate resulted in increased peroxide decomposition, while further additions of silicate resulted in the rate of decomposition being decreased. In the presence of pulp, the addition of all levels of silicate were found to reduce the level of iron catalysed peroxide decomposition. At high levels of silicate addition (>~0.008M) the iron catalysed peroxide decomposition behaviour was found to be almost identical in the presence and absence of pulp.

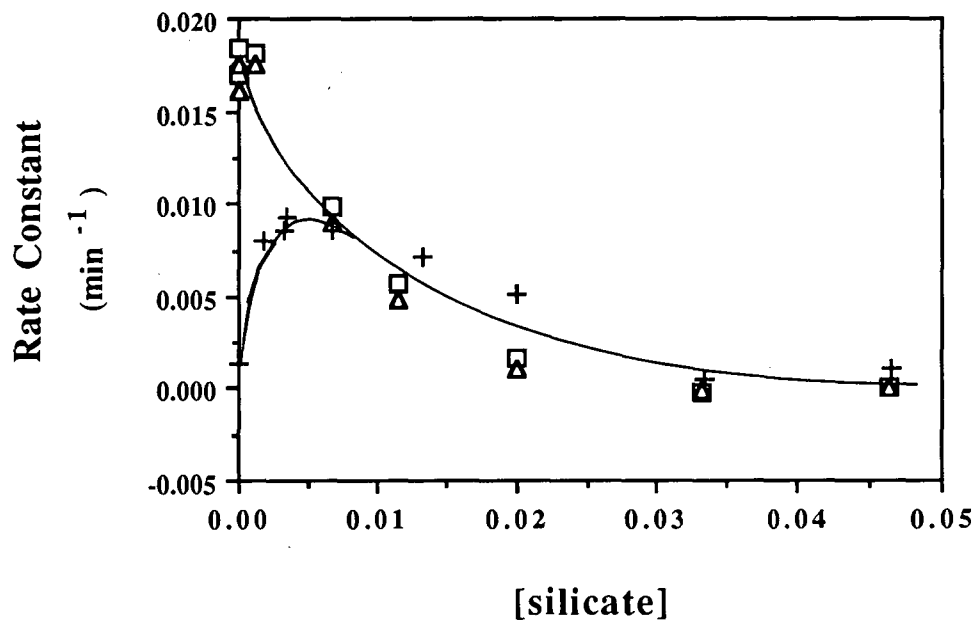

Figure 4.16 : Influence of silicate on iron catalysed peroxide decomposition in the presence of chelated TMP (Models - Δ : A , □ : B), and in the absence of pulp (+). (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$ = 0.035M, [Fe] = 8.90×10^{-6} M).

4.5.4 Effects of Magnesium on Iron Catalysed Peroxide Decomposition

The variations in first-order rate constants for iron catalysed peroxide decomposition with increasing levels of magnesium are shown in Figure 4.17. Clearly the addition of magnesium results in the stabilization of peroxide both in the presence and absence of pulp. While the stabilizing effects of magnesium on iron catalysed peroxide decomposition in the absence of pulp are well known, the dramatic decrease in the calculated first-order rate constant indicates that magnesium is also an effective additive for the reduction of iron catalysed peroxide decomposition in the presence of pulp.

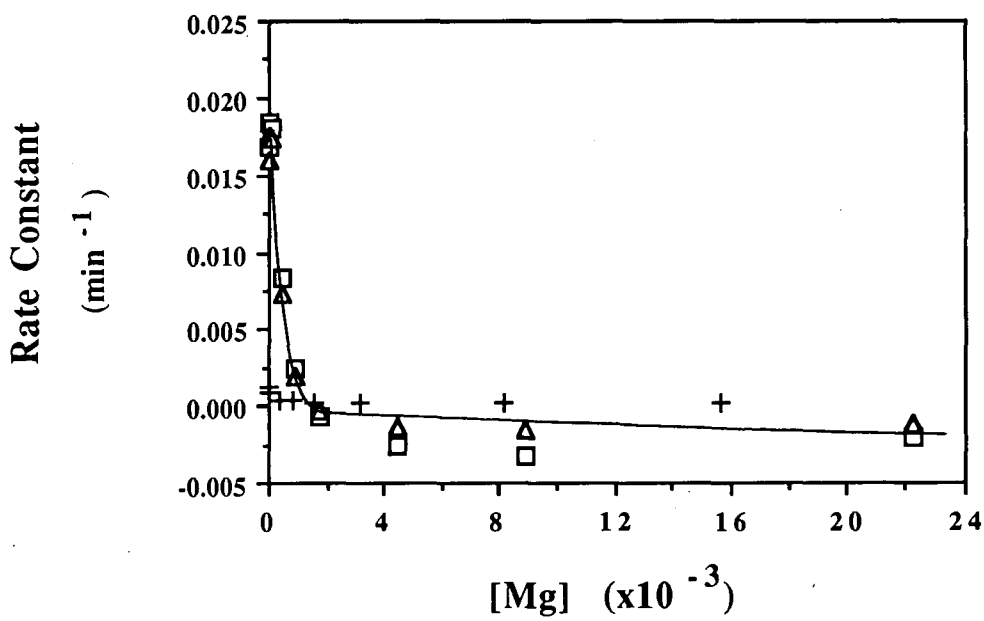

Figure 4.17 : Effects of magnesium on iron catalysed peroxide decomposition in the presence of chelated TMP (Models - Δ : A , □ : B), and in the absence of pulp (+). (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$ = 0.035M, [Fe] = 8.90×10^{-6} M).

4.6 Peroxide Decomposition in the Presence of Added Copper

Copper, together with iron and manganese, are reputed to be the most deleterious metal ions present during the peroxide bleaching of mechanical pulps[18-22,29,53]. Of these three, copper is generally present in the lowest concentrations[2,9,18,20-22,122] and is not readily removed by chelation[22,105]. It has recently been reported that in this form (ie. strongly attached to pulp) copper is not a catalyst for hydrogen peroxide decomposition[22]. These results suggest that the presence of copper should not have any major adverse effects on peroxide decomposition during bleaching. However, studies conducted in the absence of pulp have demonstrated that sodium silicate, which enjoys widespread use as an additive during peroxide bleaching, accelerates the copper-catalysed decomposition of peroxide[21,24,25]. It is therefore desirable to examine the effects of copper on peroxide decomposition during bleaching, with a particular emphasis on the effects of additives.

The effects of the addition of copper on peroxide decomposition in the presence and absence of pulp are shown in Figure 4.18. The addition of copper resulted in increased peroxide decomposition, with the rate constants approximately proportional to the concentration of added copper, both in the presence and absence of pulp. Unlike the behaviour observed in the presence of iron, it is clear from Figure 4.18 that the inclusion of pulp has little effect on the catalytic activity of copper. This implies that either the active copper species remains unchanged in the presence of pulp, or a new catalytic copper species is formed in the presence of pulp with a similar catalytic activity to the species which exists in the absence of pulp. The results of a previous study investigating the nature of copper species during bleaching, suggest that at least some of the copper forms a new species in the presence of pulp, as an increased level of soluble copper was observed in the presence of pulp (see section 3.4).

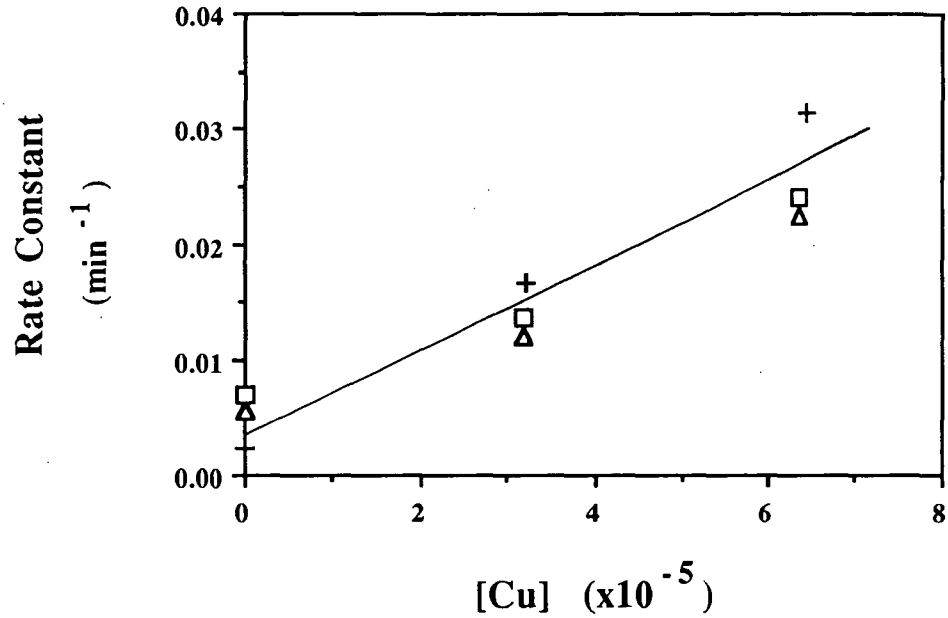

Figure 4.18 : Comparison of rates of copper catalysed peroxide decomposition in the presence and absence of chelated TMP. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2] = 0.035M$; + : no pulp, Models - Δ : A , □ : B).

4.6.1 Effects of Sodium Silicate on Copper Catalysed Peroxide Decomposition

It has previously been demonstrated that the addition of silicate to alkaline solutions containing copper can result in the formation of two complex species, one resulting in decreased peroxide decomposition, and the other in the acceleration of the decomposition rate (see section 2.4.2). Under the condition of higher temperature employed in the present study the formation of the latter species appears to be predominant as increased levels of peroxide decomposition were observed for all levels of silicate addition, Figure 4.19. In contrast, the addition of silicate to copper in the presence of chelated TMP resulted in the stabilization of peroxide, as evidenced by the decreased first-order rate constants shown in Figure 4.20. It is obvious from comparison with Figure 4.19 that the presence of pulp exerts a considerable influence

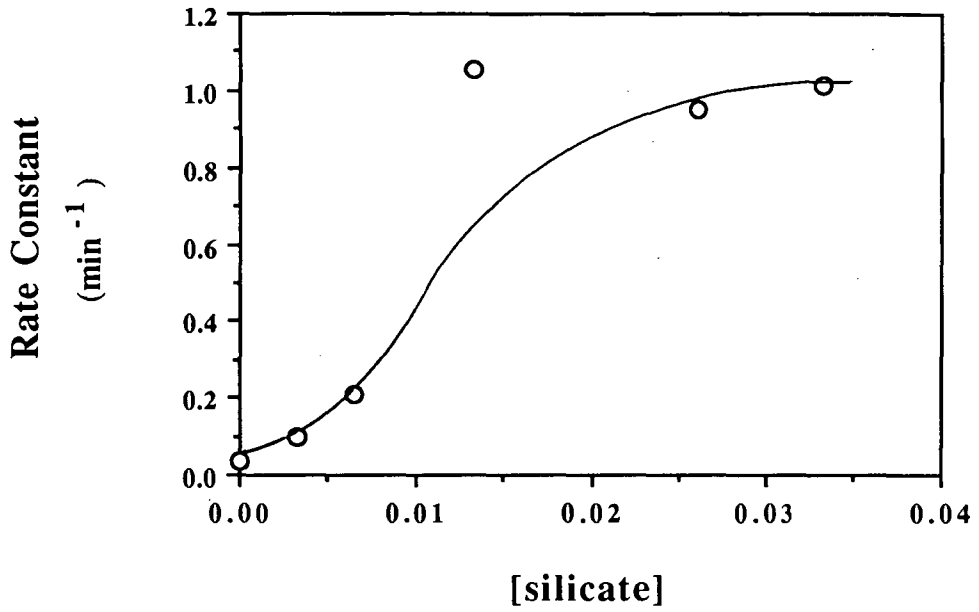

Figure 4.19 : Effects of silicate on copper catalysed peroxide decomposition in the absence of pulp. (50°C, pH 11.0, initial $[H_2O_2]$ = 0.035M, [Cu] = 6.36×10^{-5} M).

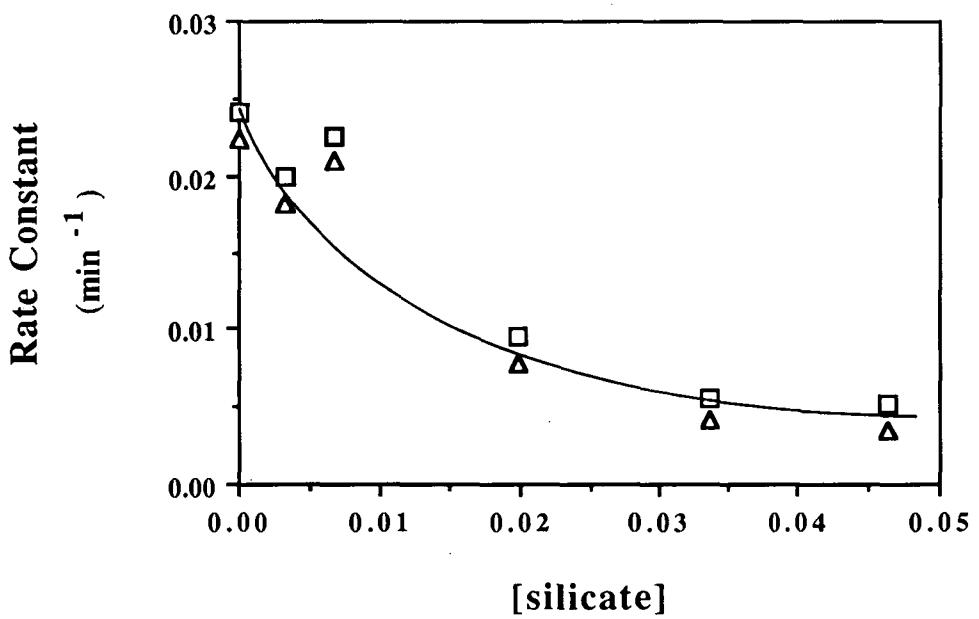

Figure 4.20 : Effects of silicate on the calculated rates of copper catalysed peroxide decomposition in the presence of chelated TMP. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$ = 0.035M; Models - Δ : A , □ : B, [Cu] = 6.36×10^{-5} M).

over the copper-catalysed peroxide decomposition behaviour in the presence of sodium silicate.

The presence of pulp was previously found to have a significant influence on the solubility of copper in the presence of silicate (section 3.4), with a much lower proportion of the added copper found to form soluble copper-silicate species. This provides direct evidence that different copper species were formed in the presence of silicate when pulp was included in the system. It seems likely that the change in the peroxide decomposition behaviour is related to the nature of the copper/silicate species present in the presence and absence of pulp.

4.6.1.1 Effects of Kraft Pulp on Peroxide Decomposition in the Presence of Copper and Sodium Silicate

A recent study has determined that copper can become strongly attached to cellulose under strongly alkaline conditions[22]. It seems possible then that the interaction of copper and the cellulose fibres present in TMP could lead to the variation in peroxide decomposition behaviour observed in the presence of sodium silicate. A strong interaction between copper and the cellulose component of the TMP could also explain the decrease in the level of soluble copper observed on the addition of silicate, in comparison with that observed in the absence of pulp (see section 3.4).

Figure 4.21 shows the comparative first-order rate constants for copper catalysed peroxide decomposition in the presence of chelated TMP, bleached kraft pulp, and in the absence of pulp, as a function of sodium silicate concentration. As was previously observed in the presence of chelated TMP, the addition of kraft pulp had little effect on the catalytic activity of copper in the absence of sodium silicate. The behaviour observed in the presence of low levels of silicate appears to be similar in the presence

and absence of kraft pulp, with increased rates of decomposition observed in both cases. However, as the silicate level was increased further the rate of copper catalysed decomposition in the presence of kraft pulp was decreased, in a manner similar to that observed in the presence of chelated TMP. In contrast, the rate of decomposition is increased further on the addition of higher levels of silicate in the absence of pulp, as shown in Figure 4.19.

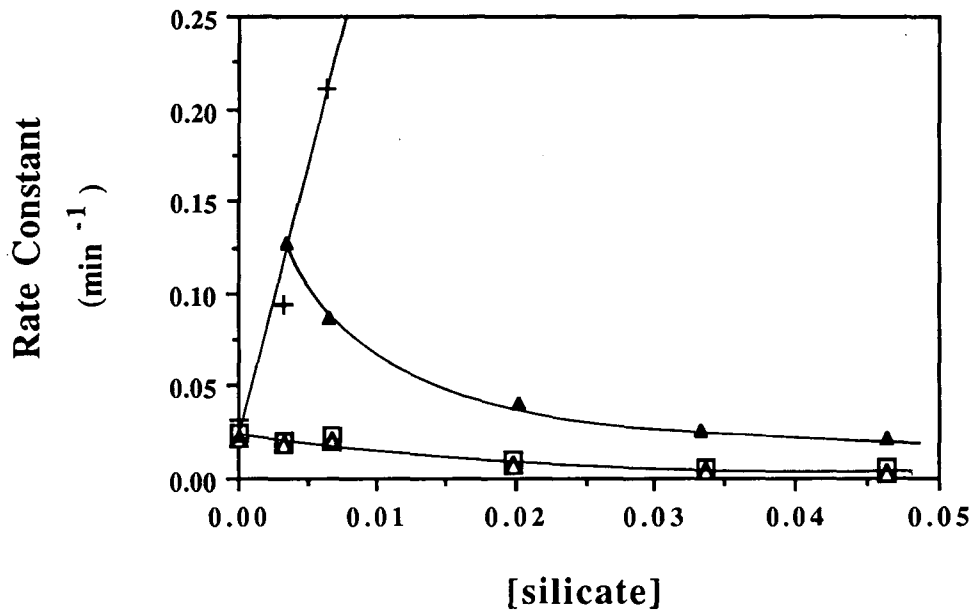

Figure 4.21 : Effect of silicate on Cu catalysed peroxide decomposition in the presence of chelated TMP (Models - Δ : A , □ : B), bleached kraft pulp (▲), and in the absence of pulp (+). (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$ = 0.035M, [Cu] = 6.36×10^{-5} M).

These results suggest that the presence of cellulose fibres can account to a large extent for the behaviour of the copper/silicate system in the presence of *P. radiata* TMP. However, the deviation in behaviour between the two pulp systems at low levels of silicate addition suggests that other components present in the TMP may also exert some influence over the copper/silicate system.

4.6.1.2 Effects of Model Compounds on Peroxide Decomposition in the Presence of Copper and Sodium Silicate

A recent study investigating the sorption of copper(II) ions on lignin has demonstrated that the metal ions can interact with a variety of lignin samples prepared by various different techniques[227]. It seems plausible then that the formation of a complex copper species through an interaction with the lignin component of the TMP could result in the modification of the peroxide decomposition behaviour in the presence of sodium silicate. In order to investigate this possibility, the effects of the inclusion of a number of aromatic model compounds on the rate of peroxide decomposition in the presence of copper and silicate have been investigated. In addition, a number of model compounds containing acidic functionalities were investigated as compounds of this type were previously found to influence the catalytic activity of iron towards peroxide decomposition (see section 4.5.2). A silicate concentration of ~0.033M was chosen, as this level of addition produced a great disparity between the behaviour of the systems in the presence and absence of pulp, as shown by comparison of Figures 4.19 and 4.20.

The results presented in Table 4.3 show that peroxide decomposition was essentially complete in a 10 minute reaction period for systems containing a wide variety of model compounds in the presence of copper and sodium silicate. In each case examined this represents a considerably enhanced degree of peroxide decomposition in comparison to the analogous copper/model systems in the absence of sodium silicate, as shown in Table 4.3. While the selection of model compounds investigated represents only a small proportion of the organic compounds likely to be present in bleaching systems in the presence of pulp, the results of the present study gave no indication these organic compounds are responsible for the modified behaviour of the copper/silicate system observed on the inclusion of pulp.

Table 4.3 : Effects of Model Compounds on Peroxide Consumption in the Presence of Copper and Sodium Silicate. (50°C, pH 11.0, initial $[H_2O_2]$ = 0.035M, [Cu] = 6.36×10^{-5} M, [Silicate] = 0.033M, [Model Compounds] = 3.6×10^{-3} M, 10 minutes reaction time).

Model Compound	Peroxide Consumption (%) after 10 minutes.		
	Model Alone	Model+Cu	Model+Cu+Si
No Model	1.0	30.6	100
Cinnamic Acid	4.1	58.1	99.3
3,4-Dimethoxycinnamic acid	6.8	38.2	99.3
4-Hydroxy-3-Methoxybenzoic Acid	6.3	45.2	99.7
3,4-Dimethoxybenzoic Acid	7.3	43.2	100
3,4,5-Trimethoxyacetophenone	7.0	54.5	99.7
Acetovanillone	4.4	51.2	99.7
Vanillin	24.4	62.5	100
Gluconic Acid	4.0	67.8	98.3
Glucuronic Acid	9.3	70.8	100
Adipic Acid	6.3	35.6	96.0
Oxalic Acid	7.0	39.2	100
Acetic Acid	1.6	27.6	100
Formic Acid	3.6	27.6	97.7

4.6.2 Effects of Magnesium on Copper Catalysed Peroxide Decomposition

The addition of magnesium to alkaline hydrogen peroxide solutions containing copper has previously been found to result in stabilization (see section 2.4.1). Figure 4.22 shows that, unlike sodium silicate, the addition of magnesium nitrate has an almost identical effect on the rate of copper catalysed peroxide decomposition in the presence and absence of *P. radiata* TMP. In both cases the addition of magnesium was observed to give almost complete stabilization.

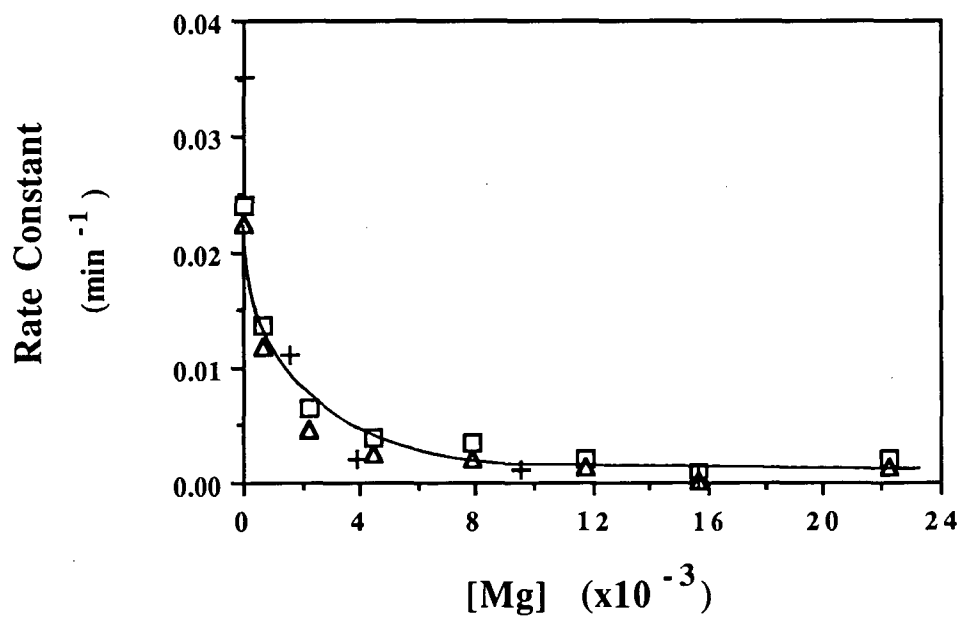

Figure 4.22 : Effects of magnesium addition on the rates of copper catalysed peroxide decomposition in the presence and absence of chelated TMP. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2] = 0.035M$; + : no pulp, Models - Δ : A , □ : B, [Cu] = 6.36×10^{-5} M).

4.7 Peroxide Decomposition in the Presence of Added Manganese

Manganese is widely considered to be the primary active peroxide decomposition catalyst present during the bleaching of mechanical pulps[9,18,22]. A number of studies investigating the effects of added manganese have also concluded that manganese is the most active of the transition metals tested in the presence of pulp[20,96]. Figure 4.23 shows the variation in first-order rate constants for manganese catalysed peroxide decomposition in the presence and absence of chelated *P. radiata* TMP. As in the case of copper, the presence of TMP appears to have little influence on the rate of manganese catalysed peroxide decomposition, with the rates found to be approximately proportional to the concentration of added manganese.

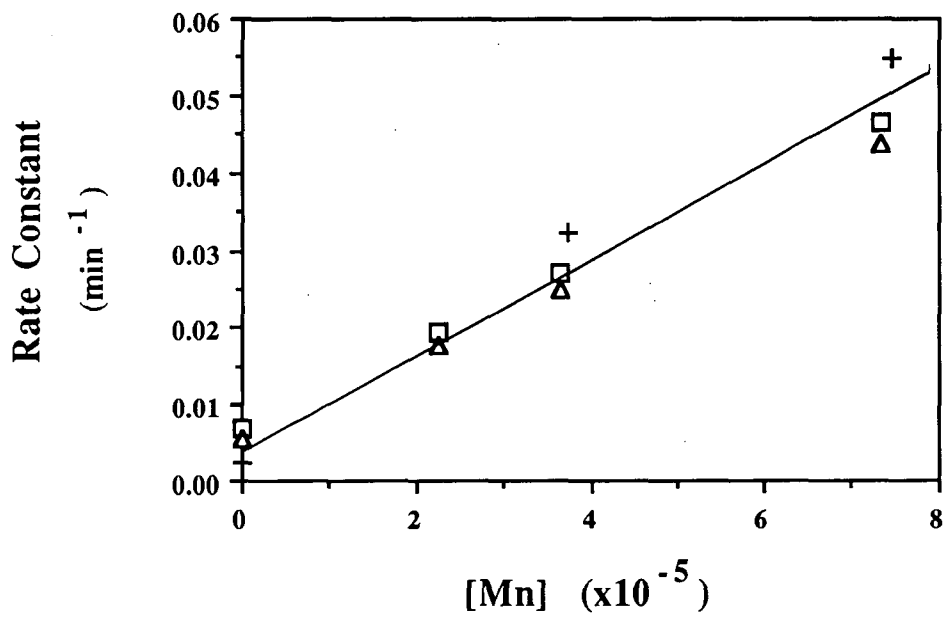

Figure 4.23 : Comparison of rates of manganese catalysed peroxide decomposition in the presence and absence of chelated TMP. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$ = 0.035M; + : no pulp, Models - Δ : A , □ : B).

4.7.1 Effects of Sodium Silicate on Manganese Catalysed Peroxide Decomposition

The effects of the addition of sodium silicate on the manganese catalysed decomposition of hydrogen peroxide in the presence and absence of pulp are shown in Figure 4.24. It is apparent from the close correlation of the first-order rate constants that the presence of pulp has little influence on the behaviour of the manganese/silicate system. In both cases, almost complete stabilization is observed at a similar optimum level of silicate addition. This result is not surprising as sodium silicate has proven peroxide stabilizing properties during the bleaching of mechanical pulps[30,31,107], where the deactivation of transition metal ions, of which manganese has been shown to be the most active, is reported to be the primary role of the silicate[24,25,27].

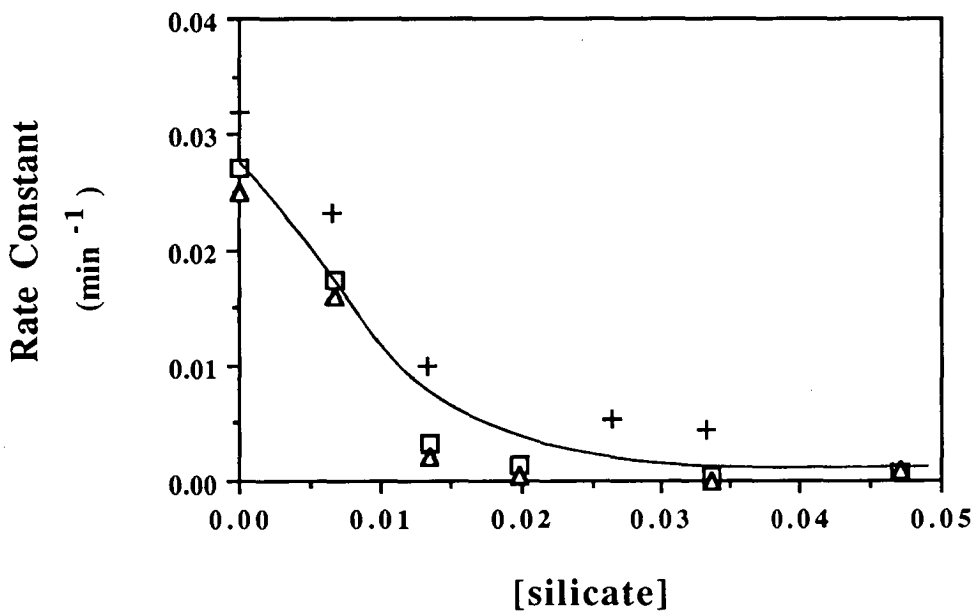

Figure 4.24 : Effects of silicate on manganese catalysed peroxide decomposition in the presence of chelated TMP (Models - Δ : A , □ : B), and in the absence of pulp (+). (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$=0.035M, [Mn] = 3.66×10^{-5} M).

4.7.2 Effects of Magnesium on Manganese Catalysed Peroxide Decomposition

Previous studies investigating the effects of the addition of magnesium to alkaline hydrogen peroxide solutions in the presence of manganese have reported an acceleration of the rate of decomposition[26,27]. Figure 4.25 shows the measured first-order rate constants for peroxide decomposition in the presence of manganese as the level of magnesium was increased. While low levels of addition resulted in increased peroxide decomposition, the addition of progressively higher levels of magnesium led to a steady decrease in the rate of decomposition. It has previously been reported that peroxide decomposition catalysts prepared by the coprecipitation of manganese and magnesium are less active than corresponding catalysts prepared by the impregnation of solid magnesium hydroxide with manganese[35]. The observed decrease in the rate constant as the magnesium level was increased can therefore be attributed to an effective decrease in the surface concentration of manganese due to the coprecipitation of $Mn(OH)_2$ with $Mg(OH)_2$. The effects of the addition of solid magnesium hydroxide on the manganese catalysed decomposition of peroxide are shown for comparison in Figure 4.26. Clearly in this case, where manganese can only form surface species on the magnesium hydroxide, the rate of decomposition was dramatically increased.

The increased catalytic activity of manganese in the presence of magnesium has previously been attributed to the formation of a new catalytic species with structural units of the type Mn-O-Mg[27]. The formation of species of this type reportedly enhances the ability of the manganese to participate in redox cycles leading to the decomposition of peroxide[27]. The results of the present study suggest that two competitive effects are important in determining the behaviour of the manganese/magnesium system in the absence of pulp. In addition to the formation of new manganese species with high catalytic activity[27], the coprecipitation of manganese

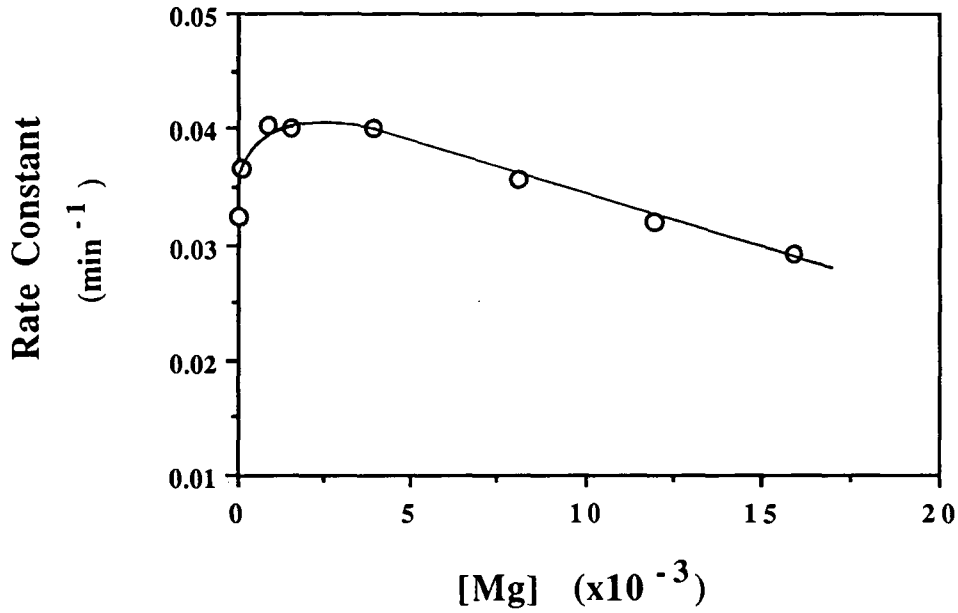

Figure 4.25 : Effects of magnesium nitrate addition on the rate of manganese catalysed peroxide decomposition in the absence of pulp. (50°C, pH 11.0, initial $[H_2O_2]$ = 0.035M, [Mn] = 3.66×10^{-5} M).

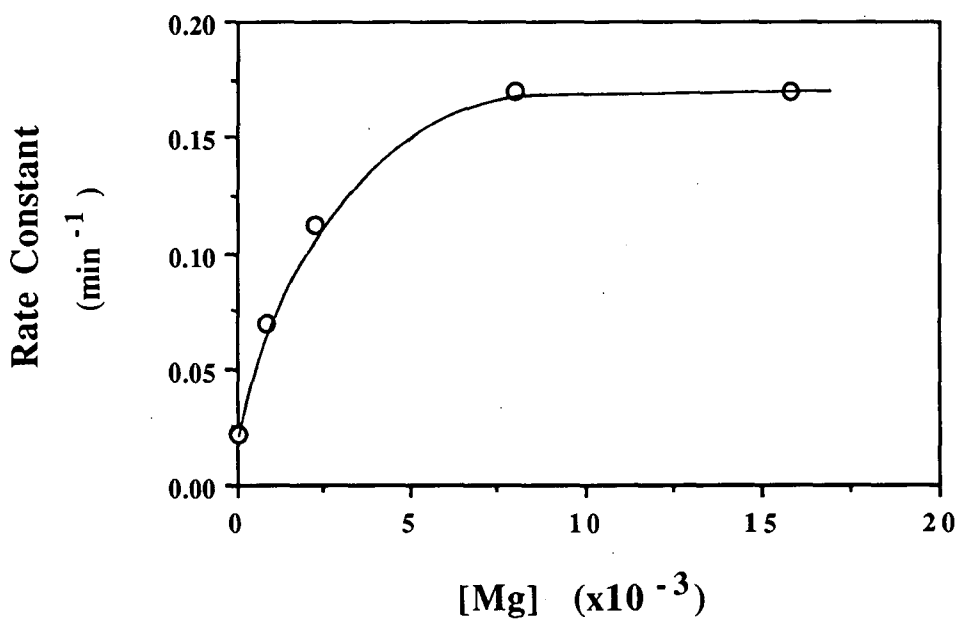

Figure 4.26 : Effects of magnesium hydroxide addition on the rate of manganese catalysed peroxide decomposition in the absence of pulp. (50°C, pH 11.0, initial $[H_2O_2]$ = 0.035M, [Mn] = 3.66×10^{-5} M).

with magnesium can result in a decrease in the amount of manganese which is available to react with peroxide. As a result a maximum catalytic activity is observed for a magnesium concentration where the majority of manganese is converted to the more active form, and yet is still available to react with peroxide.

The effects of the addition of magnesium nitrate on the rate of the manganese catalysed decomposition of hydrogen peroxide in the presence of pulp are shown in Figure 4.27. In contrast to the behaviour observed in the absence of pulp, the addition of magnesium reduced the rate of peroxide decomposition catalysed by manganese in the presence of chelated TMP. A maximum level of stabilization was found for a magnesium concentration of ~0.002M, with higher levels of magnesium addition resulting in progressively higher rates of decomposition. Clearly in the case of manganese, the isolated system does not provide a reasonable model for the stabilizing action of magnesium during pulp bleaching.

The results obtained in an earlier study investigating the solubility of metal ion species in alkaline peroxide systems indicated that the inclusion of pulp had a significant influence on the behaviour of the manganese/magnesium combination (see section 3.5). Both manganese and magnesium were found to exist solely in insoluble form when in combination in the absence of pulp, supporting the notion of the formation of a coprecipitate. However, in the presence of pulp a significant proportion of both were found to exist in soluble form. It seems likely that the change in peroxide decomposition behaviour observed on the inclusion of pulp is related to the observed change in the solubility of the catalytic species. In order to investigate this possibility further, the effects of varying the concentration of magnesium on the solubility of manganese in the presence of pulp were investigated.

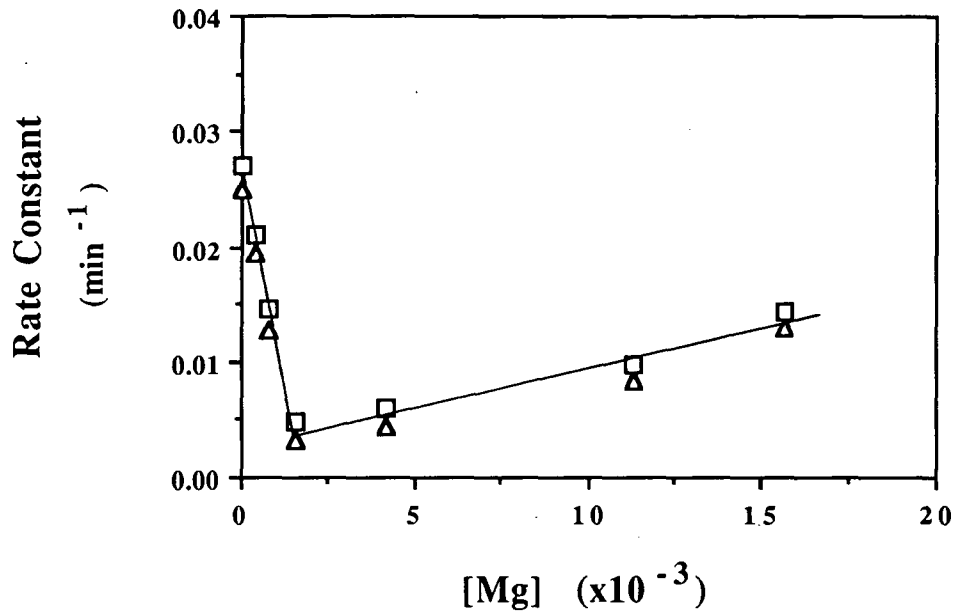

Figure 4.27 : Effects of magnesium addition on the calculated rates of manganese catalysed peroxide decomposition in the presence of chelated TMP. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$ = 0.035M ; Models - Δ : A , □ : B, [Mn] = 3.66×10^{-5} M).

Figure 4.28 demonstrates that the solubility of manganese is increased on the addition of progressively higher levels of magnesium, prior to the addition of alkali or peroxide. A similar finding has been reported to occur on the addition of aluminium to pulps containing manganese[105]. The aluminium ions reportedly compete with manganese for binding sites on the pulp, resulting in a higher proportion of manganese ions being found in solution[105]. However, for magnesium this does not appear to be the case. Figure 3.28 shows that almost all of the added magnesium remains in solution prior to the addition of alkali and peroxide. It seems more probable that the increased solubility of manganese is due to interactions with the added magnesium resulting in the formation of a soluble magnesium/manganese species.

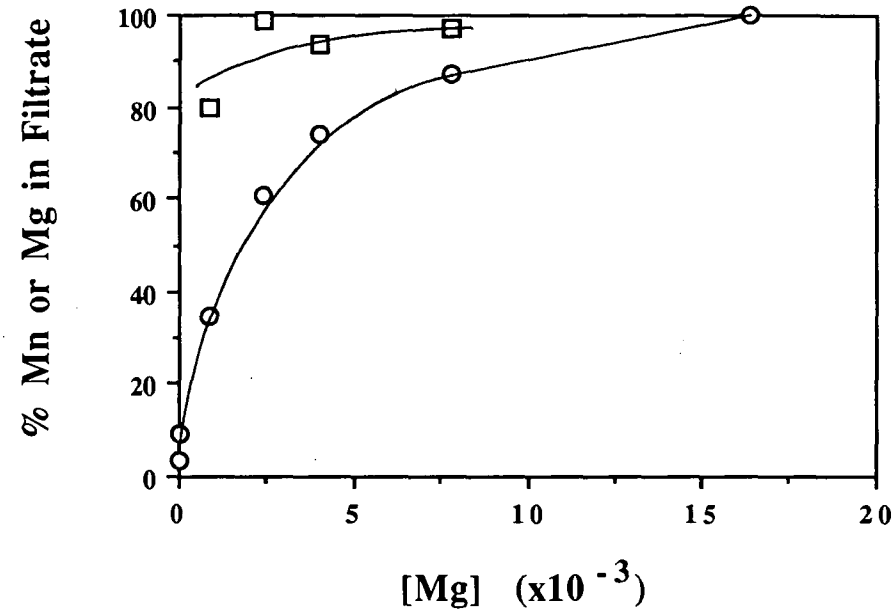

Figure 4.28 : Solubility of manganese (O) and magnesium (□) in the presence of chelated TMP at 50°C prior to the addition of alkali or peroxide.

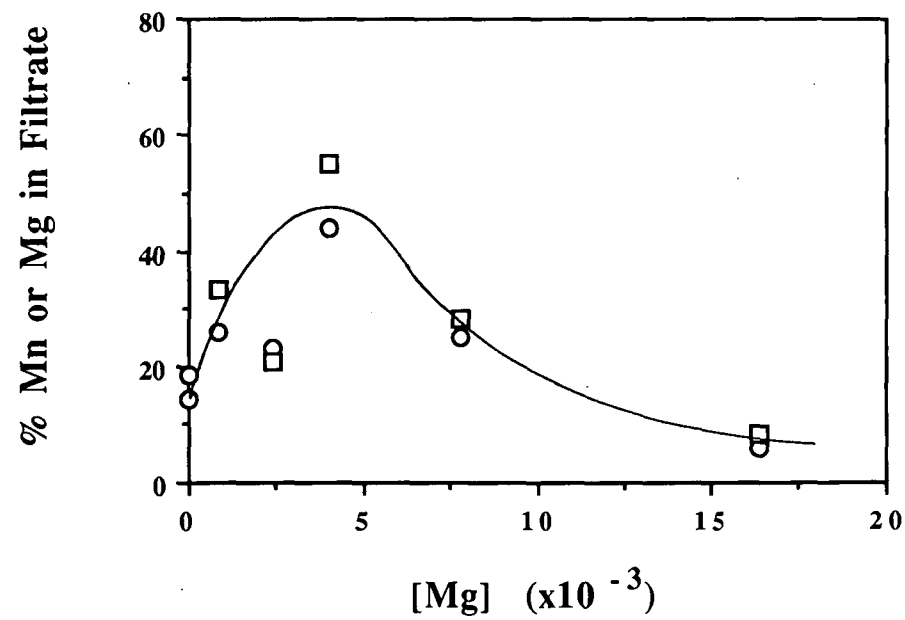

Figure 4.29 : Solubility of manganese (O) and magnesium (□) during the bleaching of chelated TMP. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$ = 0.035M, 120 min).

Figure 4.29 shows the solubility of manganese and magnesium in the presence of pulp at pH 11.0, following the addition of alkali and hydrogen peroxide. Comparison with Figure 4.27 reveals that a correlation exists between the catalytic activity observed in the presence of pulp and the presence of a soluble manganese/magnesium species. The level of magnesium required for maximum stabilization corresponds to the dose which gave the highest level of the soluble manganese species. As the magnesium level was increased above the optimum dose a decrease in the amount of soluble manganese was found, presumably through the increased proportion of manganese involved in the formation of a coprecipitate with magnesium. This may explain why the catalytic activity of manganese in the presence of pulp converges towards that observed in the absence of pulp for the addition of high levels of magnesium.

The observed differences in the solubility behaviour of the manganese/magnesium system, in the presence and absence of pulp, provides direct evidence that certain components present in the pulp can influence the form of the catalytic species present. In the case of manganese the inclusion of pulp resulted in the stabilization of peroxide following the addition of magnesium, whereas an accelerated rate of decomposition was observed in the absence of pulp. In order to further investigate the effects of pulp on the manganese/magnesium system a series of experiments were conducted examining the effects of the addition of various pulp components on the peroxide decomposition behaviour.

4.7.2.1 Effects of Kraft Pulp on Peroxide Decomposition in the Presence of Manganese and Magnesium

Previous studies have shown that under neutral pH conditions dissolved manganese salts interact much more strongly with lignin components of TMP than with carbohydrate components[147]. Figure 4.30 shows that addition of a bleached kraft pulp

to the manganese/magnesium system resulted in enhanced peroxide decomposition. It would therefore appear unlikely that the stabilising effect of magnesium during peroxide bleaching of chelated TMP in the presence of added manganese is attributable to an interaction involving the carbohydrate component of the pulp.

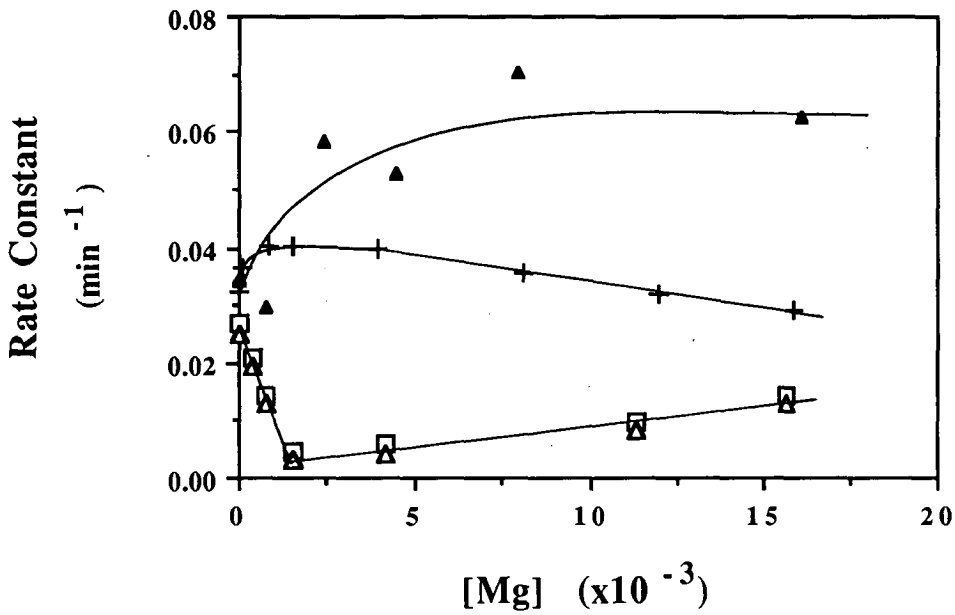

Figure 4.30 : Effects of Mg on manganese catalysed peroxide decomposition in the presence of chelated TMP (Models - Δ : A , □ : B), bleached kraft pulp (▲), and in the absence of pulp (+). (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$ = 0.035M, [Mn] = 3.66×10^{-5} M).

4.7.2.2 Effects of Model Compounds on Peroxide Decomposition in the Presence of Manganese and Magnesium

The stabilizing effects of soluble complexes of magnesium have previously been discussed in considerable detail in relation to the prevention of the peroxide decomposition reactions which lead to cellulose degradation during oxygen bleaching

reactions[115,228,229]. A study examining the oxygen treatment of a model system containing cellobiitol has shown that the generation of organic acids such as glyceric acid, glycolic acid and lactic acid gives rise to the formation of soluble magnesium complexes[228]. It has also been reported that the presence of hydroxy-acids, or products of polysaccharide degradation, in alkali media facilitates the formation of stable complexes between magnesium and transition metals[115].

During production of mechanical pulps by grinding or refining some 3-5% of the wood material is reportedly released from the fibres and becomes dissolved or dispersed in the process waters[226]. In addition, typical peroxide bleaching treatments result in a further increase in the level of dissolved and colloidal material[226]. The release of acetic acid from the deacetylation of glucomannans, together with the dissolution of acidic hemicelluloses and lignin structures are reported to contribute to the increased level of soluble species[226]. In view of the observed correlation between the level of stabilization and the solubility of manganese during bleaching in the presence of magnesium, it seems reasonable to assume that certain soluble components derived from the pulp may be responsible for the decreased peroxide decomposition observed on the addition of magnesium during bleaching in the presence of manganese.

Table 4.4 shows the effects of the addition of magnesium on the level of peroxide decomposition in the presence of manganese and a variety of model compounds. The level of magnesium chosen for study was ~4.0×10^{-3} M, as this dose produced a marked discrepancy between the behaviour observed for the manganese/magnesium systems in the presence and absence of pulp. It is clear that if the initial reaction period is considered (20 minutes), the addition of magnesium resulted in increased levels of peroxide consumption for the majority of the model systems studied, as shown in Table 4.4. However, for solutions containing manganese in the presence of gluconic

Table 4.4 : Effects of Model Compounds on Peroxide Consumption in the Presence of Manganese and Magnesium. (50°C, pH 11.0, initial $[H_2O_2]$ = 0.035M, [Mn] = $3.66x10^{-5}$ M, [Mg] = $4.0x10^{-3}$ M, [Model Compounds] = $3.6x10^{-3}$ M, 20 minutes reaction time).

Model Compound	Peroxide Consumption (%) after 20 minutes.		
	Model Alone	Model+Mn	Model+Mn+Mg
No Model	1.8	44.5	74.8
Cinnamic Acid	4.9	37.9	74.8
3,4-Dimethoxycinnamic acid	7.7	43.2	65.1
4-Hydroxy-3-Methoxybenzoic Acid	7.4	41.9	57.5
3,4-Dimethoxybenzoic Acid	7.7	43.2	71.8
3,4,5-Trimethoxyacetophenone	7.6	34.2	63.8
Acetovanillone	7.6	39.9	44.2
Vanillin	37.8	56.8	51.5
Gluconic Acid	5.6	33.6	21.6
Glucuronic Acid	15.1	38.5	28.6
Adipic Acid	6.8	50.5	56.8
Oxalic Acid	7.2	36.2	54.5
Acetic Acid	1.9	38.2	77.7
Formic Acid	4.5	45.5	74.8

acid and glucuronic acid, the addition of magnesium resulted in significantly decreased levels of peroxide consumption, apparently simulating the behaviour observed in the presence of pulp. The stabilization of iron and copper catalysed peroxide decomposition in the presence of gluconic acid and magnesium has been discussed previously[115].

In addition, the effects of the inclusion of magnesium in manganese systems containing the models vanillin, adipic acid or acetovanillone appeared to be intermediate between the behaviour in the presence and absence of pulp, with only minor changes in the levels of peroxide consumption observed. If a longer reaction period is considered (60 minutes), it is apparent that the presence of these model compounds can lead to a reduction in the level of peroxide consumption observed on the addition of magnesium, as shown in Table 4.5. However, the presence of either gluconic acid or glucuronic acid was still observed to produce the greatest reductions in the level of peroxide consumption after 60 minutes, following the addition of magnesium.

The results of the current study have demonstrated that the inclusion of organic components, representative of those which are expected to be present during the bleaching of mechanical pulps, can result in the modification of the peroxide decomposition behaviour observed for the manganese/magnesium system. The inclusion of the organic acids, gluconic acid and glucuronic acid in particular, gave results simulating the behaviour observed following the addition of magnesium to manganese in the presence of pulp. The formation of soluble complexes between magnesium[228] or transition metals[115] with organic acids, including gluconic acid[115], has previously been discussed in relation to the prevention of peroxide decomposition during oxygen bleaching reactions. Taking into consideration the observed increased solubility of manganese on the addition of magnesium in the presence of pulp (see

Table 4.5 : Effects of Model Compounds on Peroxide Consumption in the Presence of Manganese and Magnesium. (50°C, pH 11.0, initial $[H_2O_2]$ = 0.035M, [Mn] = 3.66×10^{-5} M, [Mg] = 4.0×10^{-3} M, [Model Compounds] = 3.6×10^{-3} M, 60 minutes reaction time).

Model Compound	Peroxide Consumption (%) after 60 minutes.		
	Model Alone	Model+Mn	Model+Mn+Mg
No Model	7.9	90.0	94.4
Cinnamic Acid	6.7	79.1	90.0
3,4-Dimethoxycinnamic acid	7.8	86.4	82.4
4-Hydroxy-3-Methoxybenzoic Acid	8.9	84.7	72.4
3,4-Dimethoxybenzoic Acid	12.3	85.4	87.7
3,4,5-Trimethoxyacetophenone	12.2	84.7	83.4
Acetovanillone	13.8	86.1	60.1
Vanillin	58.1	94.0	70.8
Gluconic Acid	7.1	70.4	38.5
Glucuronic Acid	35.5	80.4	38.2
Adipic Acid	9.1	95.0	83.4
Oxalic Acid	9.6	76.4	80.7
Acetic Acid	2.6	77.1	95.7
Formic Acid	4.6	92.7	92.0

section 3.5), and the correlation found between the level of soluble manganese formed on the addition of magnesium with the level of stabilization, it seems likely that the presence of the organic acid compounds leads to the stabilization of peroxide through the formation of soluble complexes with manganese and magnesium.

In addition to the organic acid systems, the inclusion of a number of other model compounds appeared to lead to reductions in the level of peroxide consumption in the presence of magnesium and manganese, particularly if longer reaction times were considered. In order to examine this effect in more detail, the behaviour of the manganese/magnesium system in the presence of the model compound vanillin was investigated in more detail.

4.7.2.3 Influence of Vanillin on Peroxide Decomposition in the Presence of Manganese and Magnesium

Solutions containing the desired levels of manganese and vanillin were prepared and allowed to age overnight to enhance their prospects of interacting. Magnesium nitrate, sodium hydroxide, and hydrogen peroxide were then added sequentially, and peroxide consumption was measured with time, at a constant pH of ~11.0. The addition of vanillin to the system containing manganese had no apparent effect on the rate of peroxide consumption as shown in Figure 4.31. However, with the introduction of magnesium a significant increase in peroxide stabilisation was found in the presence of vanillin. Figure 4.32 shows the peroxide consumption for solutions containing manganese and magnesium for various levels of vanillin addition. Low levels of vanillin addition appeared to significantly decrease peroxide consumption, while higher levels had an accelerating effect. The optimum concentration of vanillin for producing stabilization was found to be ~6.6×10^{-4} M. Excess vanillin appeared to be decomposed by the peroxide, resulting in increased consumption.

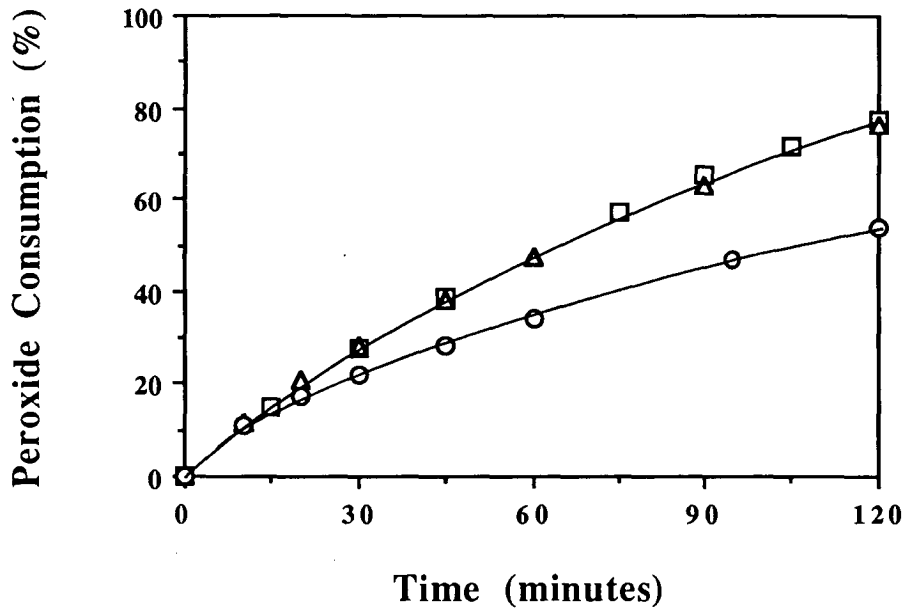

Figure 4.31 : Effect of vanillin and magnesium on peroxide decomposition in the presence of manganese. ([Mn] = 2.2×10^{-5} M, [vanillin] = 6.6×10^{-4} M, [Mg] = 7.8×10^{-3} M). □ , Mn alone ; △ , Mn+vanillin ; ○ , Mn+vanillin+Mg.

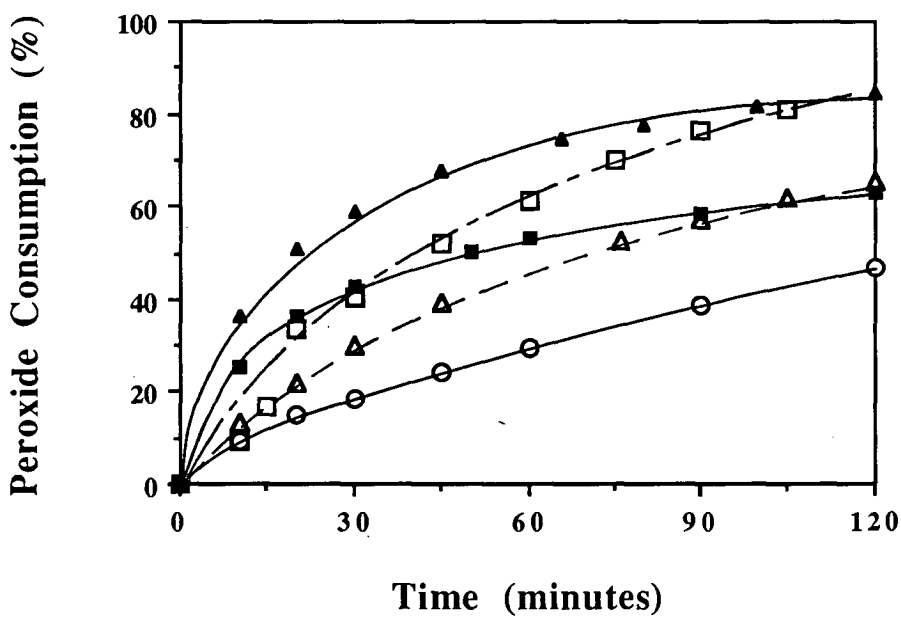

Figure 4.32 : Effects of vanillin addition on manganese catalysed peroxide decomposition in the presence of magnesium ([Mn]=2.2×10^{-5} M, [Mg]=4.0×10^{-3} M). [Vanillin] : □ , 0 ; △ , 1.3×10^{-4}M ; ○ , 6.6×10^{-4}M ; ■ , 3.2×10^{-3}M ; ▲ , 6.6×10^{-3}M.

Figure 4.33 shows the effects of magnesium dose on peroxide consumption for a system containing manganese and the optimum level of vanillin. Using this vanillin concentration, the optimum concentration of magnesium was found to be ~$4x10^{-3}$ M, as shown in Figure 4.34. Comparison with Figure 4.27 reveals that a similar concentration of magnesium was observed to give maximum stabilization of peroxide during the bleaching of chelated TMP in the presence of added manganese. Although the magnesium levels are not identical, the similar order of magnitude observed is an indication that the model system using vanillin in combination with magnesium probably has the same mechanistic characteristics as found during bleaching of pulp.

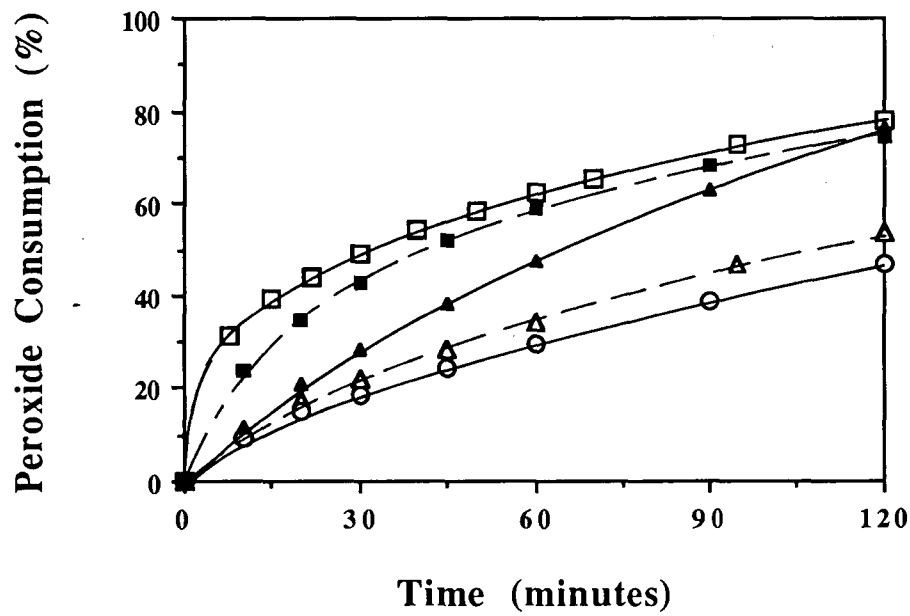

Figure 4.33 : Effects of addition of magnesium on peroxide decomposition in the presence of manganese and vanillin. ([Mn] = $2.2x10^{-5}$ M, [vanillin] = $6.6x10^{-4}$ M). [Mg] added : ▲ , 0 ; □ , $7.8x10^{-4}$ M ; ○ , $4.0x10^{-3}$ M ; △ , $7.8x10^{-3}$ M ; ■ , $4.0x10^{-2}$ M.

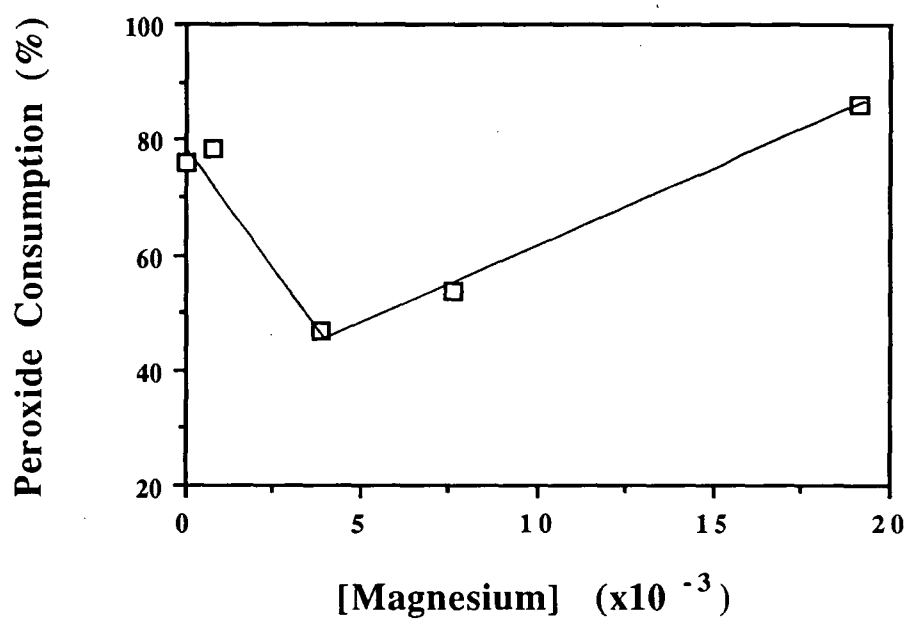

Figure 4.34 : Effects of magnesium addition on the level of peroxide consumed after 120 minutes in the presence of added manganese and vanillin. ([Mn] = 2.2×10^{-5} M, [vanillin] = 6.6×10^{-4} M).

The stabilising effects observed on the inclusion of vanillin can be attributed to an interaction involving the vanillin, or decomposition products from the vanillin, and the manganese and magnesium ions. The initial rate of peroxide consumption appears to be dependent on the amount of vanillin added, Figure 4.32, with high levels of vanillin addition giving rapid rates of consumption. This is consistent with the decomposition of vanillin by peroxide. Following the initial rapid reaction, the rate of consumption is significantly reduced and appears to be essentially independent of the level of vanillin initially added. The stabilisation observed in the presence of vanillin is therefore likely to be due to interactions between manganese, magnesium ions and a decomposition product of vanillin.

Two major reaction types are generally believed to occur[230,231], as shown in Figure

4.35. With highly stabilized peroxide solutions, a Dakin type reaction yielding methoxyhydroquinone reportedly occurs, with the perhydroxyl anion being the active species[230], Figure 4.35. The second general reaction is the oxidative degradation of the aromatic structure leading to the formation of a dicarboxylic acid by the combined effects of perhydroxyl anions and radical species formed upon the catalysed decomposition of hydrogen peroxide[230], Figure 4.35.

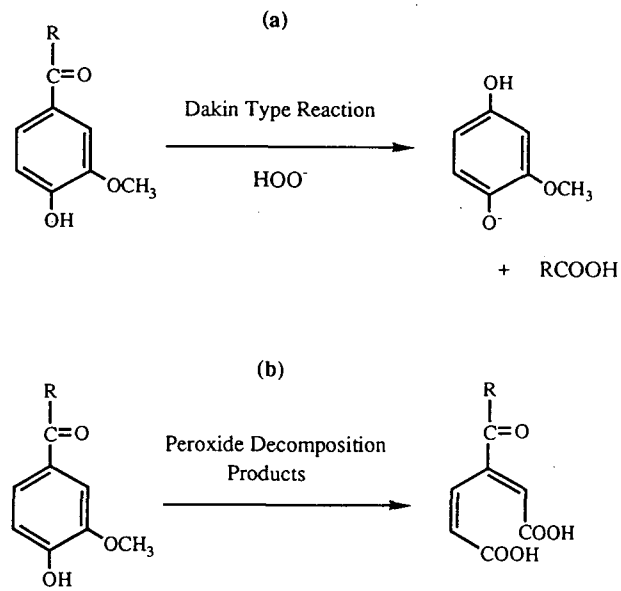

Figure 4.35 : Mechanisms for decomposition of vanillin in alkaline hydrogen peroxide. (a) Dakin type reaction, (b) dicarboxylic acid formation[230].

4.8 Summary of Transition Metal Catalysed Peroxide Decomposition

There have been a considerable number of studies investigating the effects of transition metal ions on peroxide decomposition under the conditions employed in typical bleaching applications[18-22,24-27,29,53,96,147]. These studies have been conducted both in the presence[18-22,96,147] and absence[24-27,53] of pulp to simulate the behaviour expected during peroxide bleaching reactions and in peroxide bleaching liquors respectively. However, there appears to be little consistency in the results obtained by

various workers. For example, Agnemo and Gellerstedt found that the order of activity of the transition metals in the absence of pulp was Mn > Fe > Cu[169], whereas Pero and Dence observed an order of Cu > Mn > Fe[149]. Similarly, in the presence of pulp the order of activity was found to be Mn > Cu > Fe by Kutney and Evans[96] and Read et al.[20], whereas Burton and Campbell found an order of Mn > Fe > Cu[21] and Reichert et al. found Cu > Mn > Fe[19].

In the absence of pulp, the catalytic activity of transition metals has been shown to be strongly dependent on the initial pH of the peroxide solutions[53]. For pH levels of less than ~10.8, manganese was found to be the most active catalyst, followed by copper, with iron exhibiting the lowest activity[53]. In contrast, for pH levels of greater than ~11.3, manganese appeared to be the least active of the catalytic metals, with copper exhibiting the highest activity and iron displaying intermediate activity[53]. In addition to the complex pH-activity relationship, the presence of various additives has been shown to influence the catalytic activity of the individual transition metals in differing ways[26]. It appears likely then that the variation in the catalytic behaviour observed between studies using slightly different reaction conditions can be attributed to a combination of these effects.

The present study has examined the effects of the transition metals iron, copper and manganese in the absence of additives and under simplified pH conditions (constant pH). Figure 4.36 shows that in the absence of pulp, manganese was the most active peroxide decomposition catalyst, while copper showed intermediate activity and iron showed the lowest level of activity, irrespective of whether it was added in fresh or aged form. In contrast, freshly prepared iron was found to produce the most active catalytic species in the presence of pulp, while manganese had intermediate activity and copper was the least active, as shown in Figure 4.37. Aged iron was found to be inactive in the presence of pulp.

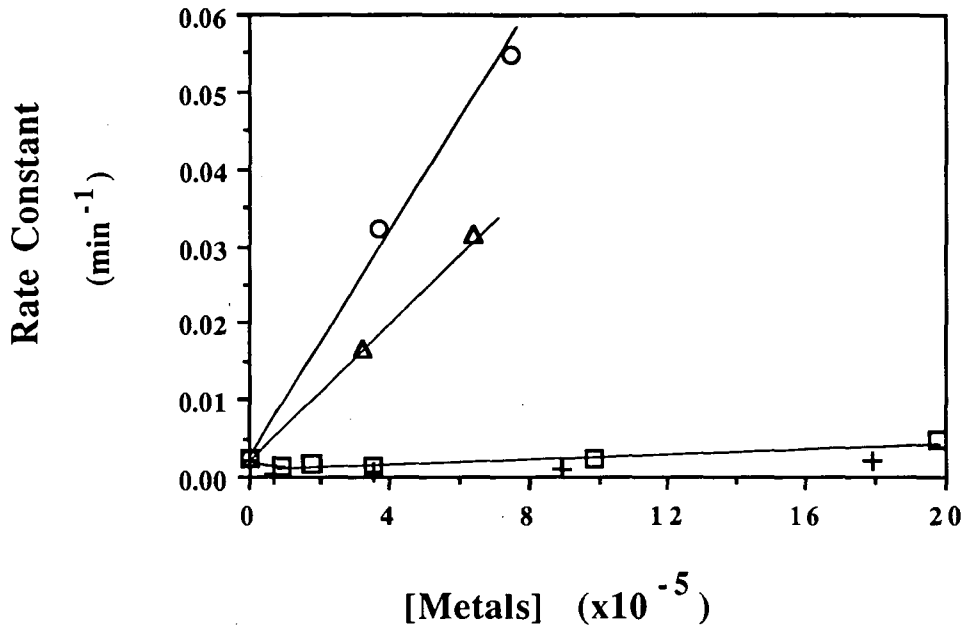

Figure 4.36 : Measured first-order rate constants for metal catalysed peroxide decomposition in the absence of pulp. (50°C, pH 11.0, initial $[H_2O_2]$ = 0.035M ; □ : fresh Fe , + : aged Fe , Δ : Cu , O : Mn).

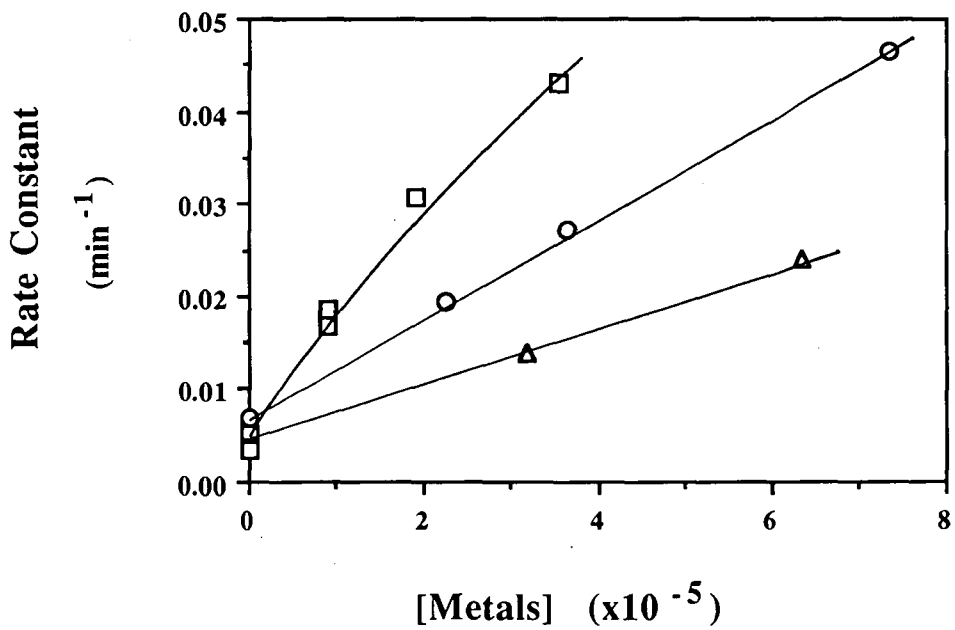

Figure 4.37 : First-order rate constants calculated using Model B for metal catalysed peroxide decomposition in the presence of chelated TMP. (50°C, pH 11.0, 4% consistency, initial $[H_2O_2]$ = 0.035M ; □ : Fe , Δ : Cu , O : Mn).

4.9 Conclusions

The rates of transition metal catalysed peroxide decomposition during the bleaching of *P. radiata* TMP, together with the effects of the additives magnesium nitrate and sodium silicate, have been evaluated with the aid of mathematical models. The use of constant pH conditions allows direct comparisons of the calculated rates with those measured for the analogous systems in the absence of pulp. The results demonstrate that the behaviour of peroxide decomposition catalysts and stabilizers during bleaching cannot be predicted by the behaviour they exhibit in the absence of pulp. The major findings of this study can be summarised as follows;

1) The stabilization of peroxide in the presence of low levels of iron can be attributed to the deactivation of the metal ion impurities which catalyse the reaction.

2) The presence of pulp greatly enhanced the catalytic activity of iron.

3) The interaction of iron with cellulose does not account for the increased activity.

4) The catalytic activity of iron was enhanced in the presence of gluconic acid or oxalic acid, suggesting that the increased activity observed in the presence of pulp may be due to the interaction of iron with carboxylic acid functionalities in the pulp.

5) The catalytic activities of manganese or copper are similar in the presence and absence of pulp.

6) The order of catalytic activity for freshly prepared samples of transition metal ions in the presence of pulp was found to be Fe > Mn > Cu, while the order in the absence of pulp was Mn > Cu > Fe.

7) Addition of magnesium to systems containing copper or iron resulted in stabilization both in the presence and absence of pulp.

8) Addition of magnesium to manganese in the presence of pulp resulted in stabilization, whereas in the absence of pulp the rate of decomposition was increased.

9) The presence of cellulose does not account for the modified behaviour observed for the manganese/magnesium system on the addition of pulp.

10) The presence of the model compounds gluconic acid or glucuronic acid resulted in the reduction of peroxide consumption following the addition of magnesium to alkaline solutions containing manganese, simulating the behaviour observed in the presence of pulp.

11) The presence of a number of other model compounds, including vanillin and acetovanillone, resulted in decreased peroxide consumption for manganese/magnesium systems, particularly at longer reaction times. Results suggest that decomposition products of these compounds may be responsible for the modified behaviour observed.

12) The increased rate of peroxide decomposition observed in the absence of added transition metals on the addition of silicate can be attributed to the formation of active catalytic species through the interaction of metal ion impurities with the silicate.

13) Addition of sodium silicate to systems containing manganese or iron produced stabilization in the presence and absence of pulp.

14) The copper catalysed decomposition of peroxide was retarded by sodium silicate during bleaching, but in the absence of pulp was accelerated.

15) The interaction of copper with the cellulose component of the pulp explains, to a major extent, the variation in decomposition behaviour observed in the presence of silicate.

16) The presence of a variety of model compounds, could not produce the modified behaviour observed for the copper/silicate system in the presence and absence of pulp.

CHAPTER 5

Effects of Peroxide Decomposition Catalysts on the Bleaching Response of *P. Radiata* TMP

5.1 Introduction

The hydrogen peroxide bleaching of mechanical pulps has been shown to be an extremely complex process, with a large number of variables capable of having a significant effect on the bleaching response[4,18,23,118]. Numerous studies investigating the effects of factors such as wood source and pulping technique, as well as bleaching variables, including pH, temperature, peroxide charge and consistency, on bleaching response have been reported[4,18,23,118]. The presence of transition metal ions has been identified as one of the major factors in determining the bleaching response[15,18-21,29,106,118,119]. These metals are thought to catalytically decompose peroxide under the alkaline conditions used during bleaching, leading to lower bleaching efficiency[15,18-21,29,106,118,119]. The importance of controlling peroxide decomposition during bleaching has motivated a number of studies investigating both the effects of various transition metal ions on bleaching[19-22,96,146,147], and the stabilizing effects of a wide range of additives[2,18,19,28-30,106,107,119].

Iron, copper and manganese have long been considered to be the transition metal ions which have the major adverse effects during the bleaching of mechanical pulps[4,18,19,118]. Supporting evidence has been provided by a wide range of studies which have demonstrated that the removal of these metals from the bleaching system results in increased bleaching responses and greater peroxide residuals[18,23]. The majority of these studies have identified manganese as having the most deleterious effects on the bleaching response, as it was found to be present in the highest quantities, and was also the most readily removed by chelation[9,18,20,22]. However, studies of this type have the disadvantage that the effects of the individual metals cannot be isolated. In attempts to overcome this deficiency a number of workers have investigated the effects of added metal ions on the bleaching response of pulps which have had the majority of the naturally occurring metal ions removed[19-22,96,146,147].

While these studies provide some insight into the relative effects of the individual metals, the interpretation of results is often complicated by the use of stabilizing agents, which may interact with different metals in different ways, in the bleaching liquors.

The removal of transition metals from the pulp prior to bleaching provides one method of increasing the efficiency of the process[2,18,106,119]. An alternative method of improving bleaching responses is through the use of stabilizing agents to reduce the level of peroxide decomposition during bleaching[19,28-30,107]. A wide range of chemicals has been tested for this purpose[30], with sodium silicate generally recognised as giving the best results[18,28,30]. It is generally accepted that the primary mechanism of stabilization by these additives is via the deactivation of the transition metals present in the pulp[25,27,30,31,107]. It is surprising then that there have been no detailed studies investigating the effects of individual additives on the peroxide bleaching of mechanical pulps in the presence of isolated transition metal ions. While a number of studies has investigated the effects of various combinations of additives and transition metals on peroxide decomposition in the absence of pulp[21,24-27], the results of the current study suggest that the presence of pulp may have a significant bearing on the observed behaviour. This implies that the results obtained in the absence of pulp may not reflect the true behaviour of the systems during the peroxide bleaching of pulp.

The current study has investigated the effects of the addition of transition metal ions on the peroxide bleaching of a *P. radiata* TMP. The pre-chelation of the pulp with DTPA prior to the addition of metal ions allows their effects to be studied in isolation. The effects of the inclusion of the additives sodium silicate or magnesium nitrate on the bleaching response in the presence of the individual transition metals have also been investigated. The results allow comparisons to be made regarding the relative effectiveness of the two additives in the presence of the individual transition metals

during bleaching. The results also enable the bleaching behaviour of the unchelated TMP in the presence of additives to be interpreted in terms of the naturally occurring transition metal ions present.

5.2 Bleaching Under Controlled pH Conditions

A number of studies investigating the kinetics of the peroxide bleaching of mechanical pulps has utilized conditions of constant pH and peroxide concentration to facilitate the interpretation of results[133,144,222]. Under these controlled conditions the rate of chromophore elimination can be defined by a kinetic expression of the type[133,144,222]:

$$\frac{-d[Chr]}{dt} = k[H_2O_2]^a[OH^-]^b[Chr]^c \qquad \text{Eq. 5.1}$$

where [Chr] represents the concentration of chromophores present. Using an expression of this type it is possible to predict the effects of changing the concentrations of reagents on the bleaching rate[133,144,222]. For a series of experiments conducted at an identical pH level, the rate of chromophore removal can be defined by a simplified expression, as the concentration of hydroxide ions is constant.

$$\frac{-d[Chr]}{dt} = k'[H_2O_2]^a[Chr]^c \qquad \text{Eq. 5.2}$$

Clearly, the rate of chromophore removal will be directly related to the concentrations of hydrogen peroxide and chromophores present at a given reaction time under these conditions. It follows that variations in the bleaching response of a given pulp sample can be related to the behaviour of peroxide decomposition catalysts and stabilizers under conditions of constant pH.

Previous studies have demonstrated that the bleaching response under conditions of

Previous studies have demonstrated that the bleaching response under conditions of constant pH is determined by the relative rates of chromophore elimination (bleaching reactions) and alkali darkening reactions[138,139]. Colodette et al. found that brightening under conditions of constant pH was less effective than conventional brightening with variable pH[139]. These workers pointed out that the decreasing pH found in conventional bleaching is advantageous, with the high initial pH allowing rapid bleaching while the concentration of peroxide is high, and the lower final pH reducing the effects of alkali darkening[139]. Martin examined the relative effectiveness of constant pH and conventional bleaching techniques at various pH levels[138]. Controlled pH was found to be advantageous at pH 10.5, where the increased bleaching rate was not countered by excessive alkali darkening[138]. However, at pH 11.5 the behaviour was found to resemble that reported by Colodette et al., with conventional bleaching found to be superior[138]. Martin found that the most effective bleaching under constant pH conditions was obtained at pH 11.0[138]. At this pH the balance of brightening reactions and alkali darkening reactions was found to be optimum for bleaching[138].

The current study has employed a constant pH of 11.0 in order to investigate the effects of transition metal ions and additives on the peroxide bleaching of a *P. radiata* TMP. The pH was maintained by the addition of semiconductor grade sodium hydroxide as required. The use of a low pulp consistency (4%) facilitated the maintenance of constant pH.

5.3 Effects of Naturally Occurring Transition Metals on Bleaching

The beneficial effects of the removal of transition metals from pulp by chelation prior to peroxide bleaching are well known[2,9,18,54,106,119]. Figure 5.1 shows that the pretreatment of *P. radiata* TMP with DTPA, followed by washing, prior to bleaching resulted in a significant reduction in the level of peroxide consumption. The increased

availability of peroxide to react with the pulp is reflected in the increased bleaching response observed for the chelated TMP shown in Figure 5.2. Figure 5.2 also demonstrates the effects of alkali darkening at the longer reaction times when the majority of the peroxide had been consumed.

Of the transition metals present in the original TMP, manganese was found to be both the most prevalent and most readily removed by chelation, as shown in Table 5.1. Manganese has previously been shown to be an active peroxide decomposition catalyst in the presence of pulp, (see section 4.7), and therefore it seems likely that the manganese originally present in TMP was a major contributing factor in the high level of peroxide consumption observed for the unchelated pulp. Similar findings have been reported by many workers investigating the effects of chelation on peroxide consumption during the bleaching of a wide variety of mechanical pulps[9,18,22].

Table 5.1 : Effects of chelation with DTPA on the transition metal content of the *P. radiata* TMP samples used in the current study.

Pulp Type	Transition Metal Content (ppm)		
	Fe	Mn	Cu
TMP	12.0 - 16.9	39.9 - 58.0	1.8 - 6.2
Chelated TMP	10.3 - 14.0	3.3 - 5.6	1.4 - 3.5

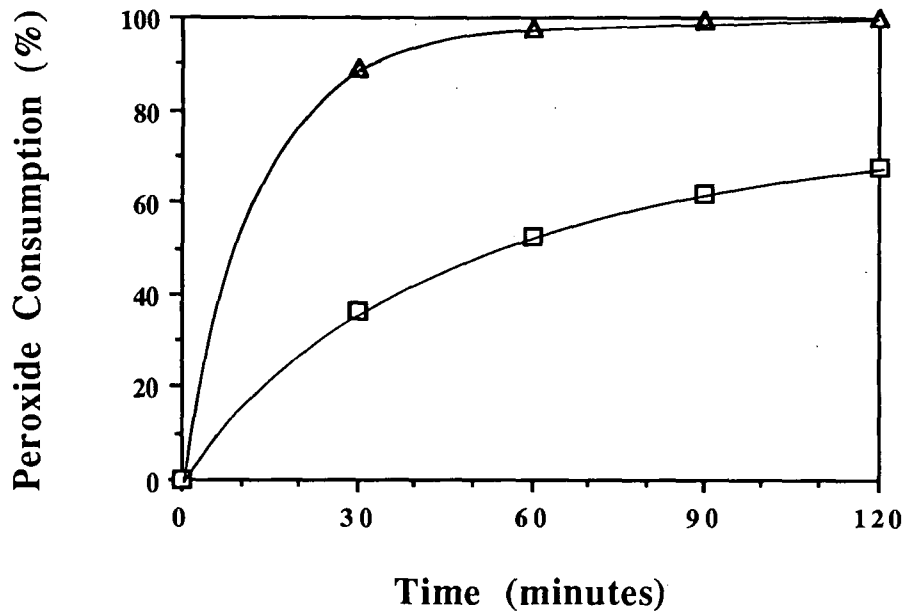

Figure 5.1 : Effects of chelation on peroxide consumption during the bleaching of *P. radiata* TMP. (△) TMP, (□) Chelated TMP.

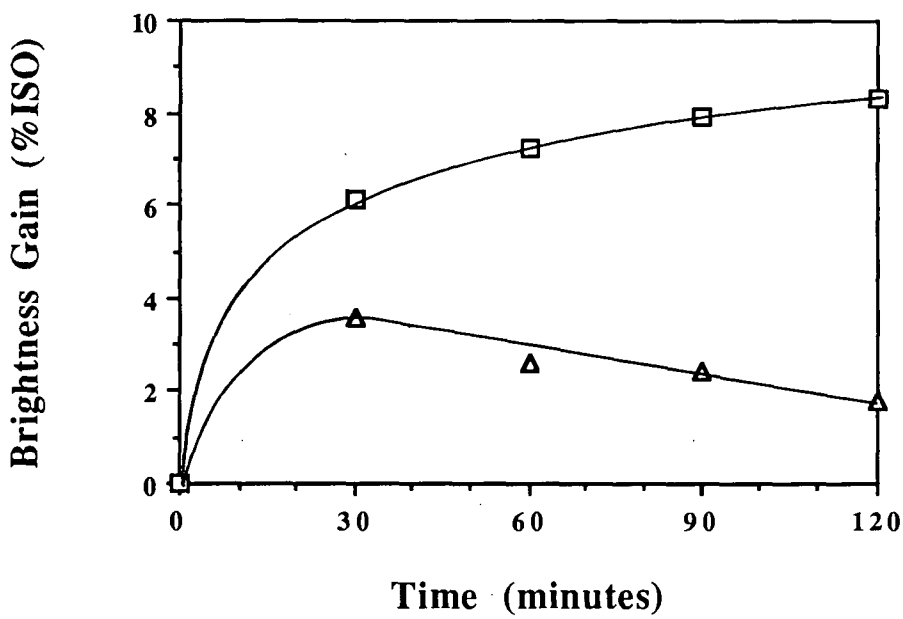

Figure 5.2 : Effects of chelation on brightness gain during the bleaching of *P. radiata* TMP. (△) TMP, (□) Chelated TMP.

In contrast to manganese, copper was only present in the original TMP in low levels, of which a significant proportion was found to be tightly bound to the pulp, Table 5.1. A previous study has established that copper which is not removed by chelation is inactive towards peroxide decomposition[22], while the present study found that fresh copper was the least active of the transition metal catalysts in the presence of pulp (see section 4.8). It is unlikely then that the naturally occurring copper has a significant influence on peroxide consumption during the bleaching of TMP.

The effects of the naturally occurring iron present during the bleaching of TMP are difficult to assess. It has been demonstrated that iron can exist in at least two forms during the bleaching of pulp. Aged iron has been found to be inactive towards peroxide decomposition, whereas freshly prepared iron is capable of forming highly active species in the presence of pulp (see section 4.5). Table 5.1 indicates that moderate levels of iron were present in the original TMP, the majority of which was found to be tightly bound to the pulp. A previous study has determined that the iron which remains with the pulp following chelation is likely to be inactive[22]. However, the results of a study of the solubility of iron during bleaching has indicated that the behaviour of the naturally occurring iron in the TMP used in the present study closely resembled that found for freshly prepared iron in the presence of chelated TMP (see section 3.6.2). In both cases the solubility of iron was found to be low in the presence and absence of magnesium, but to be increased significantly on the addition of sodium silicate. In light of the observed similarities in solubility behaviour it seems reasonable to assume that at least some of the naturally occurring iron originally present in TMP is capable of forming highly catalytically active species which contribute to the high level of peroxide consumption and poor brightness response observed in Figures 5.1 and 5.2 respectively. In addition, the observation that more iron was solubilized during bleaching in the presence of sodium silicate than was removed by the chelation process (section 3.6.2) suggests that iron which is not removed by chelation may be capable of

forming catalytically active species.

5.4 Effects of Added Transition Metal Ions on Bleaching Chelated TMP

The effects of the addition of freshly prepared iron, copper or manganese on the bleaching of chelated *P. radiata* TMP are shown in Figures 5.3 and 5.4. The concentrations of the metals used corresponded to a level of ~50ppm on o.d. pulp. It is evident that the addition of fresh samples of these transition metals resulted in both increased peroxide consumption, Figure 5.3, and decreased brightness gains, Figure 5.4. The order of the catalytic activities determined earlier for the transition metals (see section 4.8) was reflected in the respective levels of peroxide consumption. Iron led to the highest levels of consumption, followed by manganese, with copper resulting in significantly lower consumption, as shown in Figure 5.3.

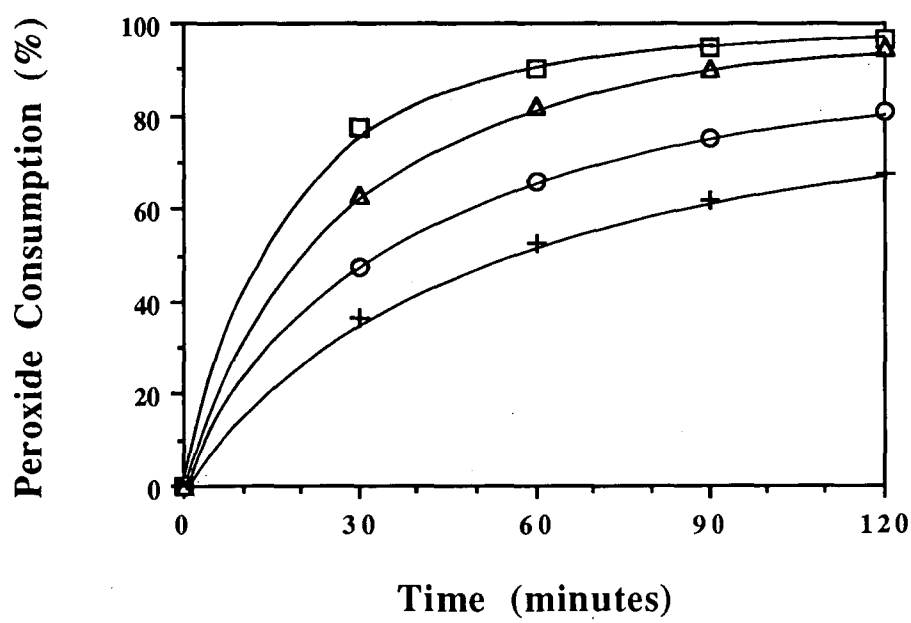

Figure 5.3 : Effects of the addition of 3.56×10^{-5} M Fe (□) , 3.18×10^{-5} M Cu (○) , or 3.66×10^{-5} M Mn (△) on peroxide consumption during the bleaching of chelated TMP (+).

This trend was also reflected in the respective brightness gains found in the presence of the transition metals, with lower brightness gains corresponding to higher levels of peroxide consumption, as shown in Figure 5.4.

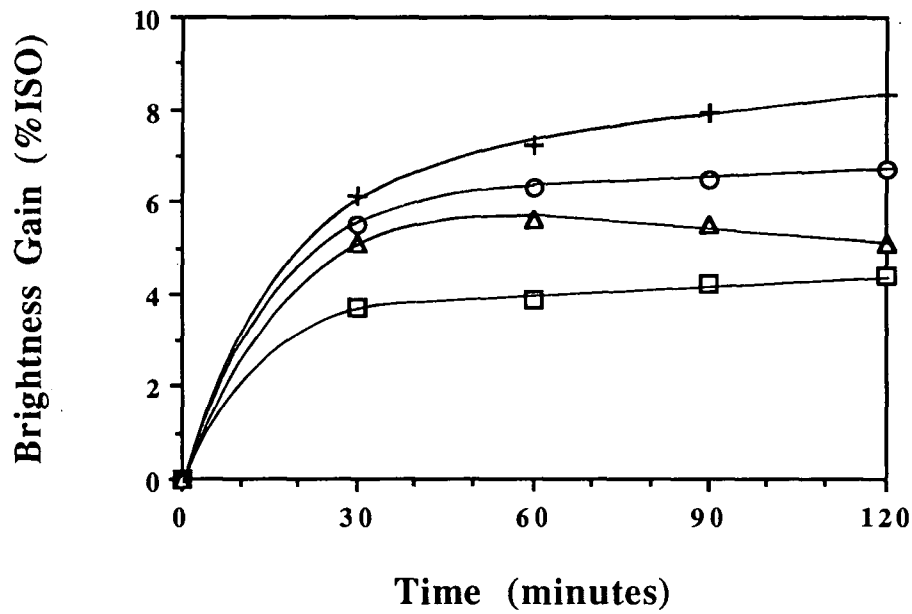

Figure 5.4 : Effects of the addition of 3.56×10^{-5} M Fe (□) , 3.18×10^{-5} M Cu (O) , or 3.66×10^{-5} M Mn (Δ) on brightness gains during the bleaching of chelated TMP (+).

The levels of added transition metal ions used in subsequent experiments investigating the effects of additives were chosen to reflect the expected behaviour of the naturally occurring metal ions present in the original TMP. Experiments examining the effects of manganese and iron on the performance of additives during the bleaching of chelated TMP employed doses corresponding to ~50 ppm and ~13 ppm on o.d. pulp respectively, as these levels approximate those of the naturally occurring metals in the TMP, as shown in Table 5.1. Figures 5.5. and 5.6 demonstrate that the addition of these concentrations of iron or manganese had a significant effect on the peroxide consumption and brightness gain respectively during the bleaching of chelated TMP. In contrast, the addition of the equivalent of ~10 ppm copper, a higher level than was

originally present in TMP, was observed to have little effect on the bleaching of chelated TMP, as shown in Figures 5.5 and 5.6. Therefore, in order to study the effects of additives on bleaching in the presence of copper it was necessary to choose a higher level of this transition metal, which was capable of having a significant influence on bleaching behaviour. Figures 5.5 and 5.6 show that the level of copper chosen for subsequent study, ~100 ppm on o.d. pulp, had a significant influence on both the peroxide consumption and brightness gain during the bleaching of chelated TMP.

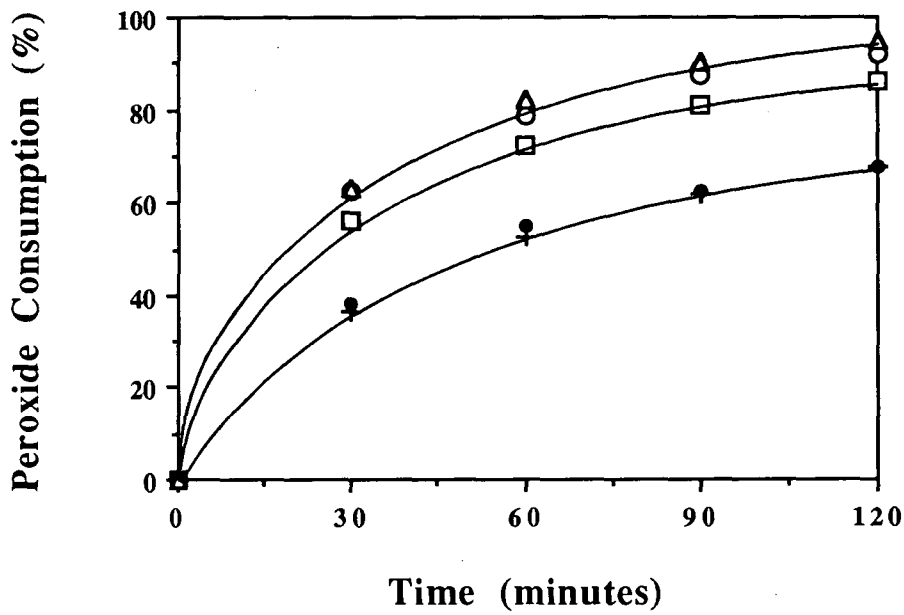

Figure 5.5 : Effects of the addition of 8.90×10^{-6} M Fe (□) , 6.46×10^{-6} M Cu (●), 6.36×10^{-5} M Cu (○) , or 3.66×10^{-5} M Mn (△) on peroxide consumption during the bleaching of chelated TMP (+).

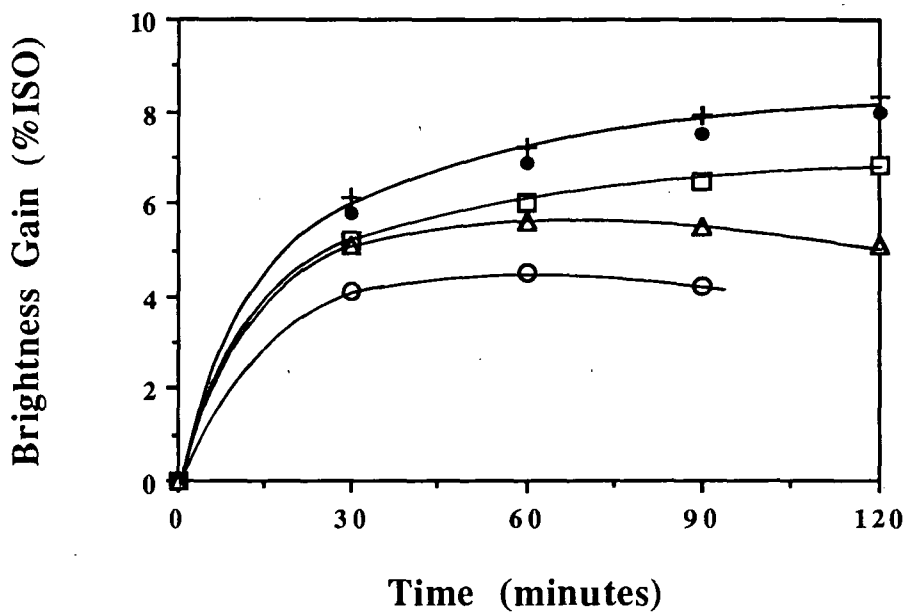

Figure 5.6 : Effects of the addition of 8.90×10^{-6} M Fe (□), 6.46×10^{-6} M Cu (●), 6.36×10^{-5} M Cu (○), or 3.66×10^{-5} M Mn (△) on brightness gains during the bleaching of chelated TMP (+).

5.5 Sodium Silicate as an Additive in the Bleaching of Mechanical Pulp

While the beneficial effects of sodium silicate in industrial bleaching formulations have long been recognised[118], much confusion has surrounded the exact mechanisms by which it operates[25,28,107,165]. Early studies attributed the benefits obtained using silicate to its ability to perform in a number of roles including as a detergent, penetrant, buffer, stabilizer and corrosion inhibitor[118]. Silicate has also been reported to increase the bleaching ability of peroxide through the formation of peroxo-silicate species[108]. However, it is generally accepted that the primary role of sodium silicate during bleaching is the stabilization of hydrogen peroxide through the deactivation of transition metal ions[25,107]. The ability of silicate to perform in other roles, and the relative importance of these functions remains the topic of much

discussion[28,30,107,160-164].

The results of a recent study have demonstrated that the benefits obtained using sodium silicate are directly related to the efficiency of the chelation process[139]. The greatest benefits were obtained for an unchelated pulp, while the bleaching performance of a regularly chelated pulp was also improved, but to a lesser extent[139]. Another study of the effects of chelation on the effectiveness of silicate during bleaching attributed approximately 50% of the benefit obtained to the deactivation of the transition metal ions present in the unchelated pulp[107]. The beneficial effects observed for the bleaching of pre-chelated pulps implied that silicate must have at least one other role[107]. However, the addition of silicate to a "superchelated" pulp, which had undergone exhaustive metal ion removal processes, had little effect[139]. This result demonstrates that the addition of silicate is only beneficial when the metal catalysed decomposition of peroxide is responsible for a lowering of the bleaching efficiency.

The role of silicate as a buffer has been discussed in a number of recent publications[28,30,107,162]. While silicate has been shown to exhibit the characteristics of a buffer, the importance of this function during bleaching is not clear[28,30,107,162]. In the present study the buffering effects of silicate are circumvented by the use of constant pH conditions, allowing the stabilizing properties to be studied in isolation.

5.5.1 Effects of Sodium Silicate on Bleaching *P. radiata* TMP

Figures 5.7 and 5.8 show the effects of sodium silicate addition on the bleaching of chelated and unchelated *P. radiata* TMP. As expected, the addition of silicate resulted in decreased peroxide consumption, Figure 5.7, which was accompanied by increased brightness gains, Figure 5.8. The results indicate that the addition of silicate to TMP can be equally, if not more, effective than removal of metal ions by chelation under

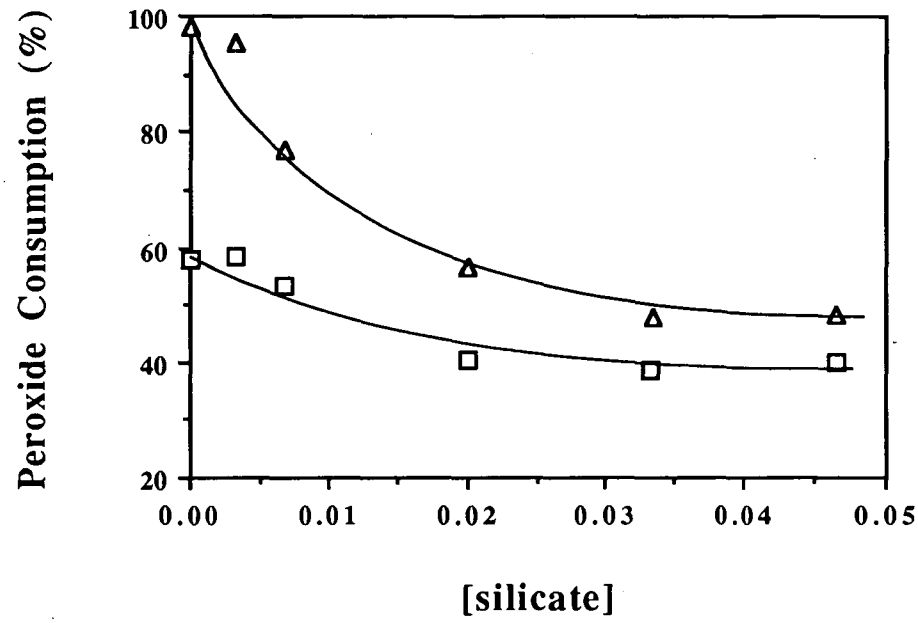

Figure 5.7 : Effects of sodium silicate on peroxide consumption during the bleaching of chelated (□) and unchelated (Δ) *P. radiata* TMP. Reaction time = 120 minutes.

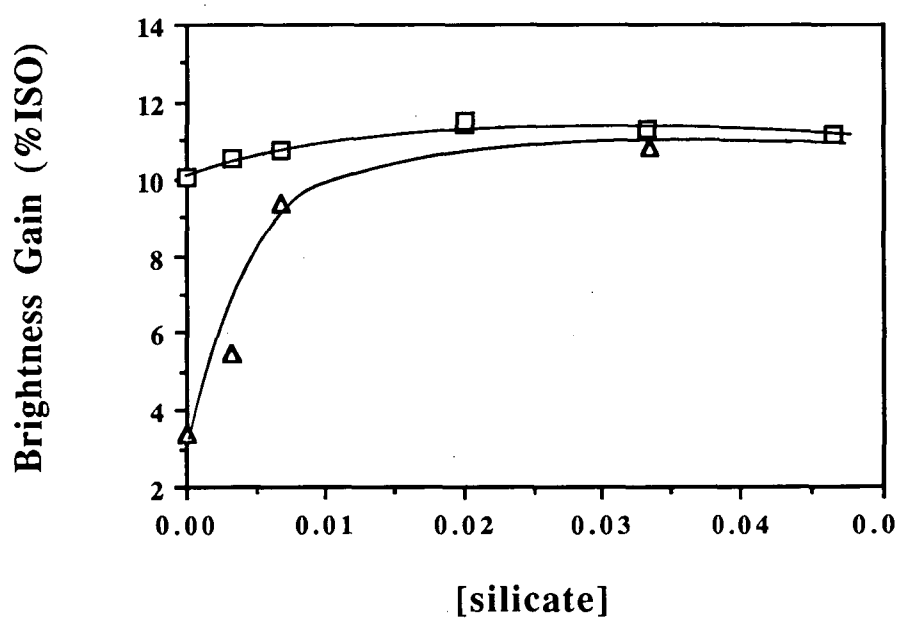

Figure 5.8 : Effects of sodium silicate on brightness gains following the bleaching of chelated (□) and unchelated (Δ) *P. radiata* TMP. Reaction time = 120 minutes.

conditions of constant pH. The best bleaching results under the current conditions were obtained by adding sodium silicate to the pre-chelated pulp. The significant reduction in peroxide consumption observed suggests that some catalytically active metals must still be present during the bleaching of the chelated TMP.

Examination of Figure 5.7 reveals that the pre-chelation of pulp has little effect on the level of silicate required to produce the maximum stabilization of peroxide. It has previously been reported that a lower silicate dose is required when bleaching chelated pulp compared to a pulp which has not been pretreated[107]. However, it is difficult to determine the reason for this effect as the bleaching experiments were conducted under industrial conditions with "optimum" alkali charges for each level of silicate[107]. The chelation process results in a decrease in the level of metal ions present, and therefore any change in the optimum silicate dose would be expected to relate directly to the metal ion concentrations in the bleaching system. It is therefore of interest to examine the effects of the individual transition metal peroxide decomposition catalysts on the behaviour of sodium silicate during bleaching.

5.5.2 Effects of Sodium Silicate on Bleaching in the Presence of Added Transition Metal Ions

It has previously been determined that the addition of sodium silicate results in decreased catalytic activities for iron, copper and manganese in the presence of chelated TMP (see sections 4.5.3, 4.6.1, and 4.7.1 respectively). Figure 5.9 shows that peroxide consumption was decreased for the bleaching of chelated TMP in the presence of added metals as the silicate dose was increased, reflecting the decreased catalytic activities of the added transition metals in the presence of silicate. An increase in the brightness gains was observed corresponding to the decreased levels of peroxide consumption, as shown in Figure 5.10.

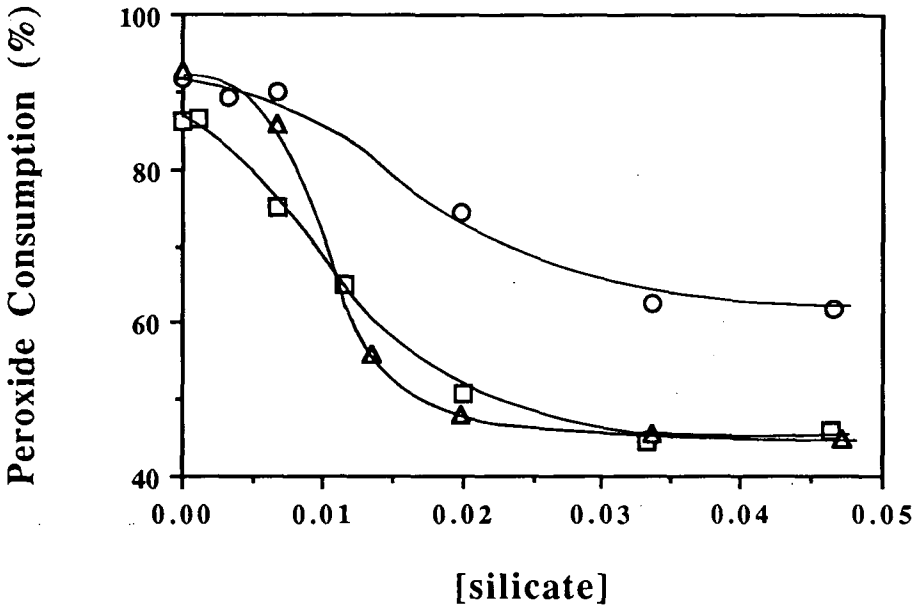

Figure 5.9 : Effects of sodium silicate on peroxide consumption during the bleaching of chelated TMP in the presence of 8.90×10^{-6} M Fe (□), 6.36×10^{-5} M Cu (○), or 3.66×10^{-5} M Mn (△). Reaction time = 120 minutes.

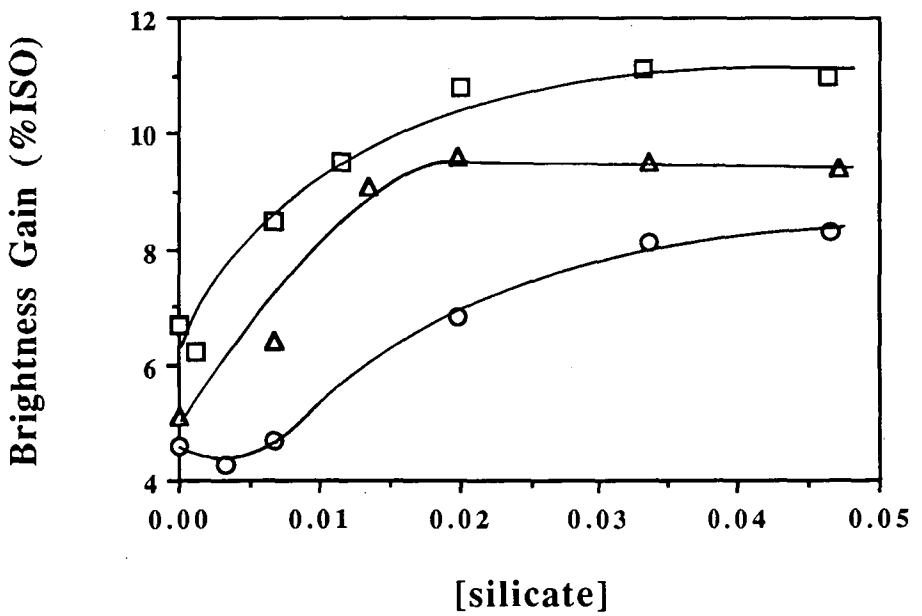

Figure 5.10 : Effects of sodium silicate on brightness gains following the bleaching of chelated TMP in the presence of 8.90×10^{-6} M Fe (□), 6.36×10^{-5} M Cu (○), or 3.66×10^{-5} M Mn (△). Reaction time = 120 minutes.

The results shown in Figure 5.9 indicate that a similar level of sodium silicate was required for maximum peroxide stabilization, irrespective of which transition metal ions were present. As the removal of metal ions by chelation was also observed to have little effect on the optimum silicate dose, it would seem that the the ratio of silicate to metal ions is not an important consideration in determining the behaviour of the systems in the presence of pulp. An alternative method of effectively changing the metal ion concentrations is to vary the pulp consistency in the bleach systems. As industrial peroxide bleaching is conducted over a wide range of pulp consistencies it is of interest to determine what effect this variable has on the behaviour of silicate as a stabilizing agent.

5.5.3 Effect of Pulp Consistency on the Stabilization of Peroxide by Sodium Silicate

The following results for bleaching experiments conducted at 1 and 4% consistency were obtained using the same levels of chemical additions, pH (constant) and total volume, but with the amount of pulp varied. Results obtained at 12% consistency under conditions of variable pH are also given for comparison. The level of silicate addition can be represented as either a concentration in solution or a percentage on pulp.

The peroxide consumption behaviour observed during the bleaching of unchelated TMP at different consistencies in the presence of sodium silicate is shown in Figures 5.11 and 5.12. The results show that the concentration of silicate in solution required to give optimum peroxide stabilization was independent of the pulp consistency, and thus the metal ion concentrations, as shown in Figure 5.11. As a consequence, the silicate dose required, represented as the percentage of silicate on pulp, decreases as the pulp consistency increases, as shown in Figure 5.12. These results are consistent

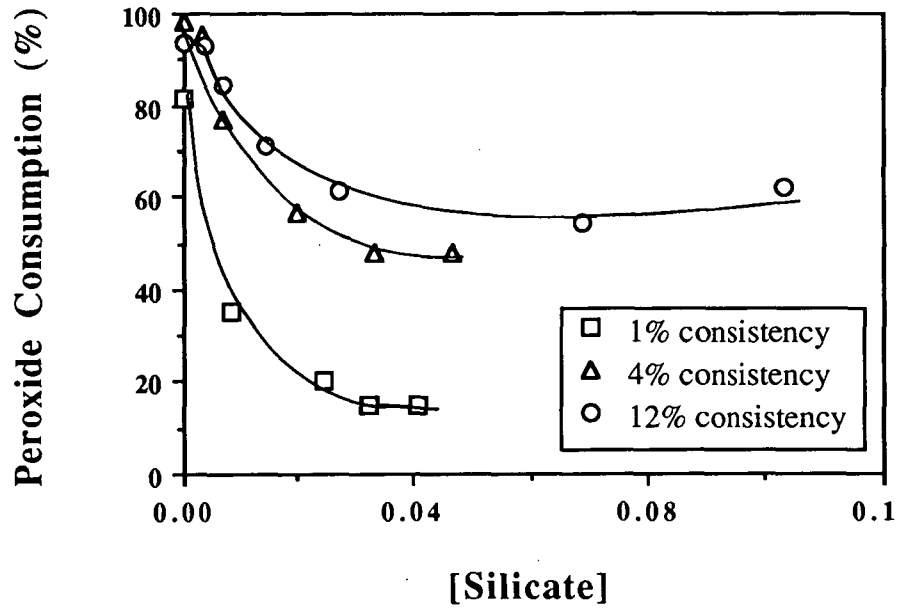

Figure 5.11 : Effect of pulp consistency on peroxide consumption during bleaching of *P. radiata* TMP in the presence of sodium silicate. Silicate dose represented as a concentration in solution. Reaction time = 120 minutes.

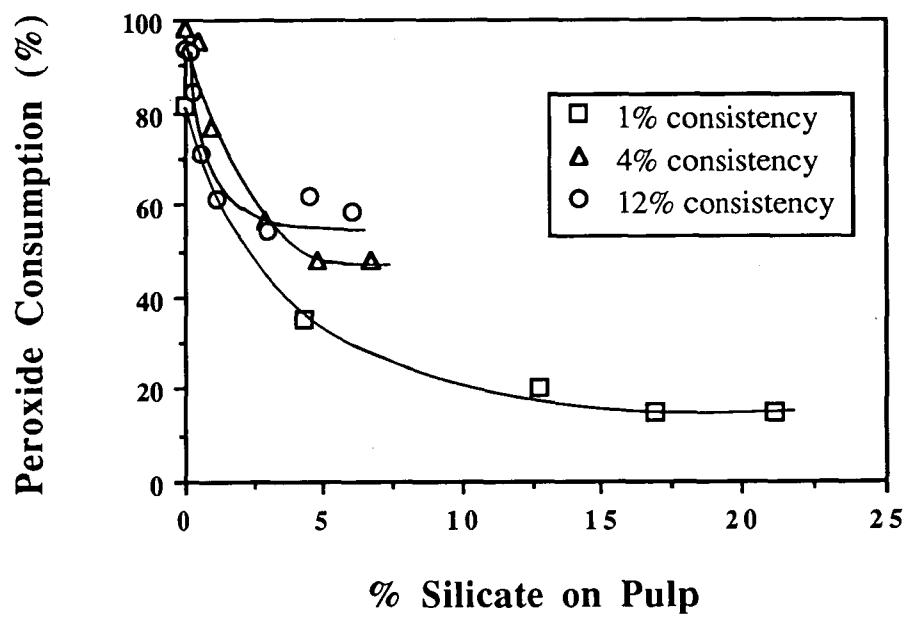

Figure 5.12 : Effect of pulp consistency on peroxide consumption during bleaching of *P. radiata* TMP in the presence of sodium silicate. Silicate dose represented as a percentage on pulp. Reaction time = 120 minutes.

with the findings of a study conducted under industrial conditions which indicated that the percentage of silicate on pulp required for optimum bleaching is lower at higher pulp consistencies[107].

5.6 Magnesium as an Additive in the Bleaching of Mechanical Pulp

The stabilizing effects of magnesium salts on peroxide bleaching liquors are well known, with small doses capable of almost completely retarding decomposition reactions[4,26,28]. Epsom salt, magnesium sulfate, enjoys widespread use as a bleach liquor stabilizer, particularly when the liquor is to be stored prior to use[4,28]. Many studies have also reported the effects of magnesium on the catalytic activity of various transition metal ions in alkaline peroxide solutions[24,26,27]. Magnesium has been found to stabilize peroxide in solutions containing iron[26] and copper[26], while accelerating the rate of decomposition in the presence of manganese[26,27] and silver[24]. A polarographic study has established that magnesium does not interact with peroxide, but rather the magnesium interacts with the metal ion catalysts and thus influences the activity[114]. The present study has also demonstrated that a correlation exists between the formation of magnesium/metal ion complexes, measured by absorbance, and the catalytic activities of the systems (see sections 2.3.1 and 2.4.1). A study of the effects of magnesium on the solubility of transition metal ions also indicated that direct interactions between the magnesium and the metals occurred (see sections 3.3, 3.4 and 3.5). The major role played by magnesium in influencing the decomposition of peroxide in alkaline solutions can therefore be attributed to direct interactions between the magnesium and the metal ions present.

The use of magnesium in the pulp and paper industry is not restricted to the peroxide bleaching area. Magnesium is also an important additive in oxygen bleaching processes, where it protects cellulose against degradation[110-112,114-116,228,229,232].

The primary role of the magnesium has been shown to be the stabilization of peroxides formed as intermediates during the reaction, thus inhibiting the formation of radical species which are thought to be responsible for the carbohydrate degradation[110,111,114-116,229]. The mechanism by which the magnesium operates has been demonstrated to be through the deactivation of catalytic transition metal ions present in the pulp[111,114,115,233]. Despite the obvious differences between oxygen bleaching of chemical pulps and peroxide bleaching of mechanical pulps, the role of magnesium appears to be similar in each case. During oxygen bleaching magnesium is successfully used to deactivate transition metal ions resulting in a decrease in carbohydrate degradation[111,114,115,233]. Despite its proven ability to modify the catalytic activity of transition metal ions in the absence of pulp[24,26,27], typical doses of magnesium have been found to have no effect on peroxide bleaching of mechanical pulps in the absence of sodium silicate[28,31]. However, it has recently been reported that higher than usual doses of magnesium can have an effect during bleaching[167]. Additional results have demonstrated that magnesium can have a significant influence on the catalytic activities of transition metals in the presence of pulp (see sections 4.5.4, 4.6.2 and 4.7.2). The present study has re-evaluated the use of magnesium as a peroxide stabilizer during the bleaching of mechanical pulp.

5.6.1 Effects of Magnesium on Bleaching *P. radiata* TMP

Examination of the literature on the use of magnesium to inhibit cellulose degradation during oxygen bleaching reveals that the doses of magnesium salts required can be much higher than those typically used in peroxide bleaching formulations[114,229]. In addition, results indicate that the solubility of the magnesium can have a significant influence on its effectiveness[115,228,229,233]. In the present study magnesium nitrate was used, as it could be obtained in high purity, and was previously shown to influence the catalytic activities of transition metal ions in the absence of pulp (see

sections 2.3.1 and 2.4.1). The magnesium was added to the pulp in soluble form prior to the addition of alkali or peroxide to enhance the probability of its interaction with metal ions bound to the pulp[233].

Figures 5.13 and 5.14 show the effects of magnesium nitrate addition on the bleaching of TMP and chelated TMP. The addition of magnesium to give concentrations of up to ~2.5×10^{-3} M, or ~0.15% magnesium on pulp, clearly resulted in decreased peroxide consumption for both the unchelated and chelated pulps, as shown in Figure 5.13. However, as the magnesium dose was increased further, the peroxide consumption increased when bleaching the unchelated TMP, while little change was observed for the chelated TMP over the same range of magnesium additions, Figure 5.13. It appears likely that the increase in peroxide consumption observed at high levels of magnesium addition is directly attributable to the loosely bound transition metals present in the unchelated TMP, as the effect was absent when bleaching chelated TMP, from which a significant proportion of the transition metals had been removed prior to bleaching, as shown in Table 5.1. The decrease in peroxide consumption observed on the addition of magnesium to chelated TMP suggests that some catalytically active metal species must be present during the bleaching of the pre-treated pulp.

The brightness gains obtained from the bleaching experiments conducted in the presence of added magnesium are shown in Figure 5.14. Low levels of magnesium addition resulted in improved brightness gains for both the TMP and chelated TMP. However, it was observed that as the magnesium dose was increased, the brightness gains fell off dramatically. While this behaviour could be attributed to the increased peroxide consumption found for these levels of magnesium addition in the presence of unchelated TMP, it cannot account for the decreased brightness gains observed for the chelated TMP where the level of peroxide consumption was essentially unchanged. Clearly the behaviour with respect to brightness gains during bleaching in the presence

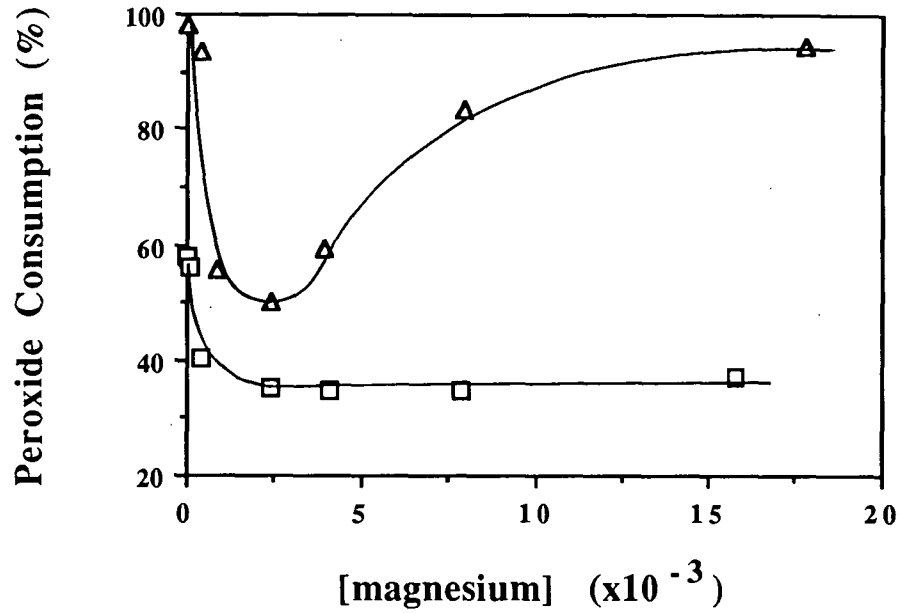

Figure 5.13 : Effects of magnesium on peroxide consumption during the bleaching of chelated (□) and unchelated (△) *P. radiata* TMP. Reaction time = 120 minutes.

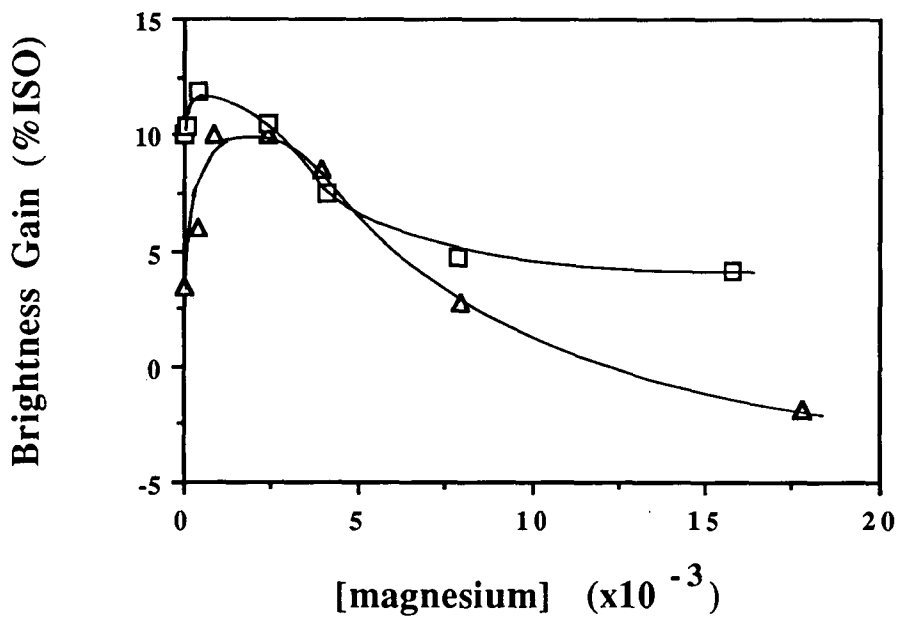

Figure 5.14 : Effects of magnesium on brightness gain following the bleaching of chelated (□) and unchelated (△) *P. radiata* TMP. Reaction time = 120 minutes.

of magnesium does not simply relate to the degree of peroxide stabilization achieved.

As was observed in the case of sodium silicate, the level of magnesium required for optimum stabilization was found to be similar for both the chelated and unchelated pulps, indicating that the level of transition metals is not an important consideration in determining the optimum dose of the additive. However, the removal of metal ions by chelation did result in a significant deviation from the peroxide consumption profile observed for the unchelated TMP as the magnesium dose was increased, Figure 5.13. This suggests that the transition metals present in the TMP play an important role in defining the peroxide consumption behaviour during bleaching in the presence of magnesium. In order to investigate the role of individual transition metals on the bleaching response in the presence of magnesium, the effects of the addition of iron, copper and manganese on the bleaching of chelated TMP have been examined.

5.6.2 Effects of Magnesium on Bleaching in the Presence of Added Transition Metal Ions

The effects of magnesium nitrate on the stabilization of peroxide during the bleaching of chelated TMP in the presence of added transition metal ions are shown in Figure 5.15. The addition of magnesium, to give concentrations of up to ~2-4x10^{-3} M, resulted in reduced levels of peroxide consumption in the presence of each of the transition metals investigated. Further increases in the magnesium dose had little additional effect on peroxide consumption during bleaching in the presence of iron or copper. However, in the presence of added manganese the addition of high levels of magnesium resulted in increased levels of peroxide consumption. The similarity of the effects of magnesium addition on the peroxide consumption behaviour observed for bleaching unchelated TMP (Figure 5.13) and chelated TMP enriched with manganese (Figure 5.15) is consistent with the widely held view that manganese is the

predominant peroxide decomposition catalyst present during the bleaching of mechanical pulps.

Figure 5.16 shows the corresponding brightness gains achieved for bleaching chelated TMP enriched with transition metals in the presence of magnesium. In each case, a maximum brightness gain was found for a magnesium concentration of ~2.5×10^{-3} M, which corresponds to the optimum level required for peroxide stabilization, as shown in Figure 5.15. As the magnesium dose was increased above this level, the brightness gains achieved were observed to drop off significantly, irrespective of which transition metal was present, Figure 5.16. The fact that this effect was observed both in the presence of manganese, where peroxide consumption increased, and iron or copper, where the level of peroxide consumption was virtually unchanged, indicates that the decreased brightness gains observed at high doses of magnesium are not simply related to the concentration of peroxide present during bleaching.

Bleaching experiments conducted both in the presence and absence of added transition metals have demonstrated that the addition of high levels of magnesium results in a decrease in the brightness gains achieved. As the decreased bleaching response has been shown not to be related to the level of peroxide consumption, and was found to occur irrespective of the presence or absence of transition metal ions, it appears likely that the magnesium itself may be responsible for the observed behaviour. The inclusion of magnesium nitrate in the bleaching system resulted in an increase in the alkali charge required to bring the pH to 11, presumably due to the formation of insoluble magnesium hydroxide. While magnesium hydroxide is unlikely to discolour the pulp itself, being a white solid, it seems likely that the additional alkali charge is related to the observed darkening effect.

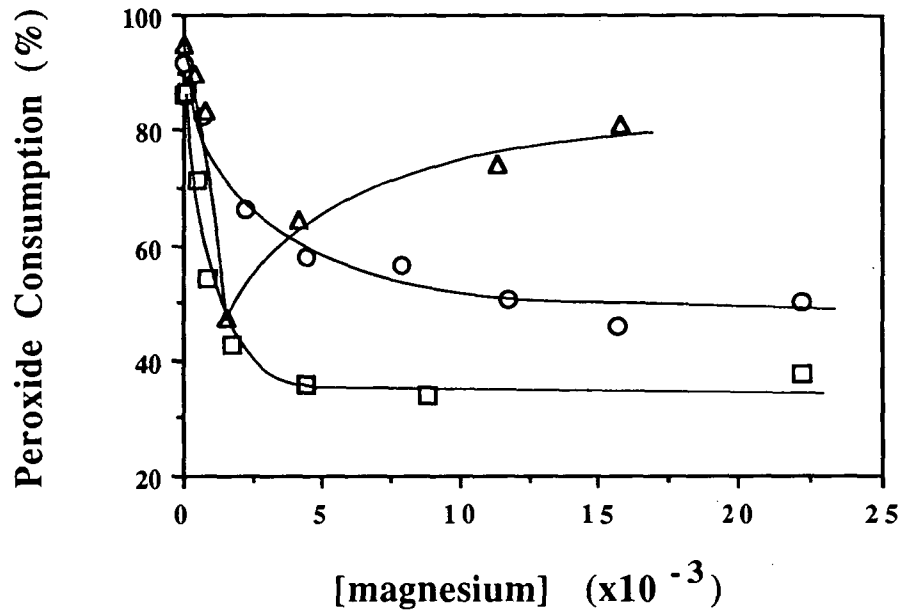

Figure 5.15 : Effects of magnesium on peroxide consumption during the bleaching of chelated TMP in the presence of 8.90×10^{-6} M Fe (□), 6.36×10^{-5} M Cu (○), or 3.66×10^{-5} M Mn (△). Reaction time = 120 minutes.

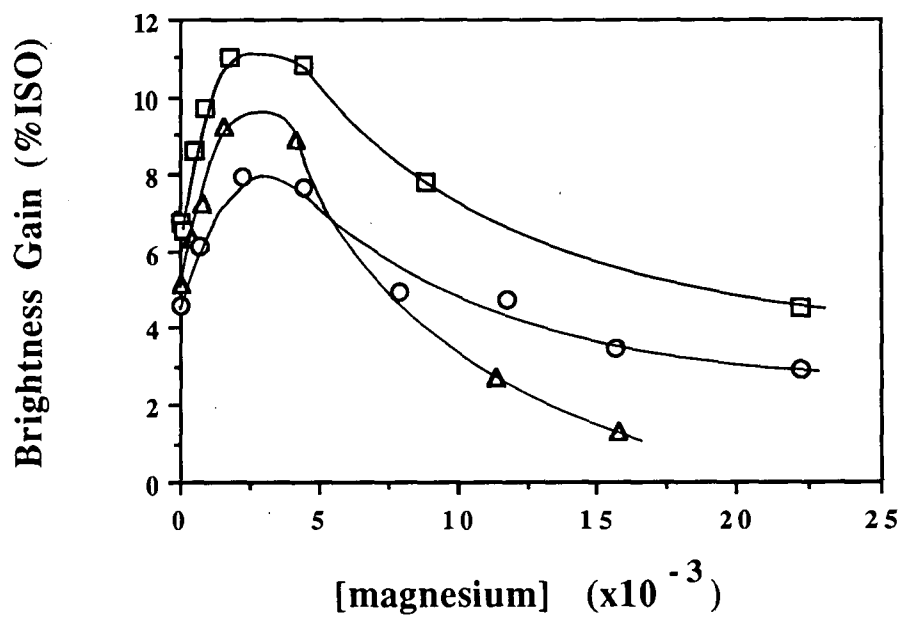

Figure 5.16 : Effects of magnesium on brightness gains following the bleaching of chelated TMP in the presence of 8.90×10^{-6} M Fe (□), 6.36×10^{-5} M Cu (○), or 3.66×10^{-5} M Mn (△). Reaction time = 120 minutes.

5.6.3 Effects of Magnesium Hydroxide Formation on Bleaching TMP

Alkali darkening is a well known phenomenon and is the subject of many studies in the literature[140-142]. While the effects of alkali darkening are usually seen at the latter stages of bleaching when little or no peroxide remains, it has been reported that rapid darkening can also occur at the beginning of the reaction[141]. The rate of alkali darkening is generally believed to be directly related to the free hydroxide concentration, ie. pH[140,141], while certain metals are also reported to influence the reaction[96]. In the present study the pH is maintained at a constant level over the course of the reaction, so the changes in bleaching response cannot be attributed to changes in the free hydroxide ion concentration.

Visual inspections of pulp bleaching formulations in the presence of high levels of magnesium suggest that colour formation (darkening) occurs in the initial phase of the reaction. This is clearly reflected in the bleaching curves for chelated pulp in the presence of magnesium shown in Figure 5.17. The brightening profiles are almost identical for each level of magnesium addition, with the exception of an initial displacement which appears to be dependent on the level of magnesium addition. In order to investigate the darkening effect further, a bleaching experiment was carried out using solid magnesium hydroxide as the additive. The results, together with those of an experiment with an identical level of magnesium added as the nitrate salt, are shown in Figure 5.18. Identical brightness curves are obtained irrespective of the form in which the magnesium was added. However, the brightness of the initial samples, taken after the addition of magnesium but prior to the alkali or peroxide, indicates that the presence of magnesium hydroxide resulted in the pulp darkening considerably, whereas no darkening occurred with the magnesium nitrate until after the addition of alkali. This implies that the magnesium hydroxide is in some way responsible for the darkening effects observed during bleaching.

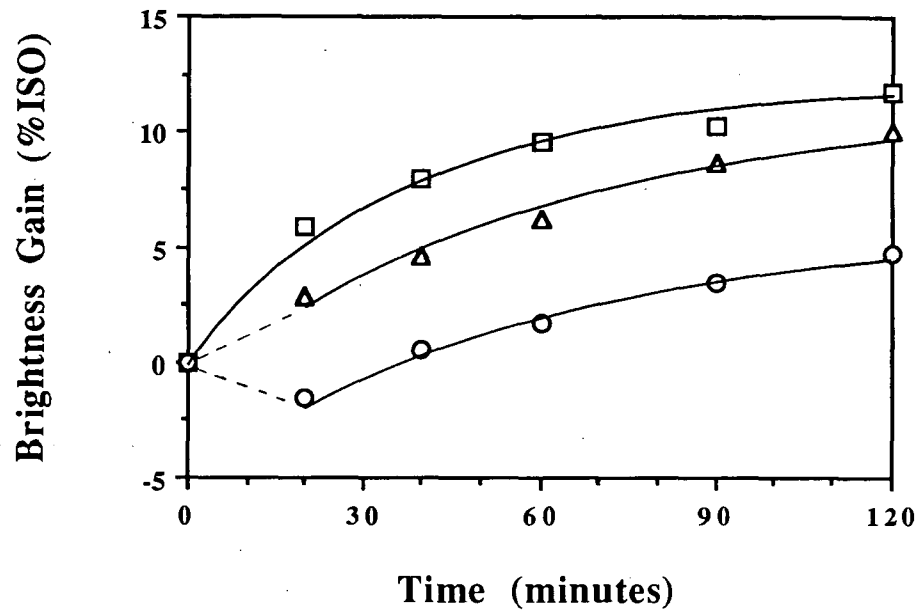

Figure 5.17 : Effects of magnesium nitrate on brightening responses observed for the bleaching of chelated *P. radiata* TMP. Magnesium concentrations : (□) 4.0×10^{-4} M, (△) 2.4×10^{-3} M, (○) 7.9×10^{-3} M.

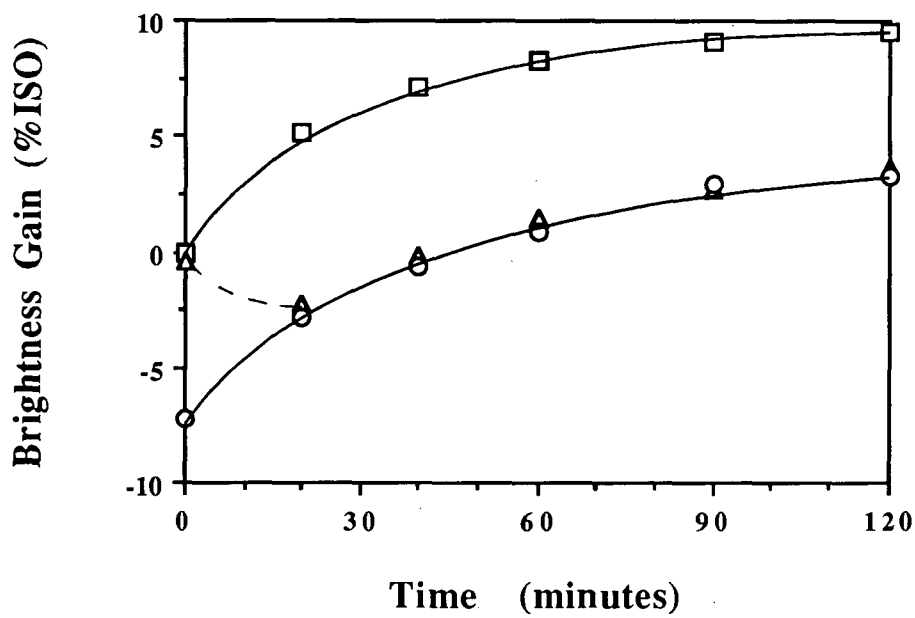

Figure 5.18 : Effect of magnesium source on bleaching responses observed for chelated *P. radiata* TMP. (□) no magnesium added : [Mg] = 1.78×10^{-2} M added as : (△) magnesium nitrate ; (○) magnesium hydroxide.

The darkening effects of magnesium hydroxide were examined further by adding identical levels of hydroxide, as either sodium hydroxide or magnesium hydroxide, to chelated TMP in the absence of peroxide, Figure 5.19. Similar levels of brightness loss were observed in both cases, despite the large discrepancy in the measured pH values, Figure 5.20. Previous studies have reported that alkali darkening does not occur at pH levels of less than ~10[140,142]. However, this is clearly not the case in the presence of magnesium hydroxide, where the brightness loss was found to be comparable to that observed in the presence of an identical level of sodium hydroxide, despite the pH being significantly lower than 10. These results suggest that the hydroxide bound to magnesium, while not contributing to the measured pH, is capable of participating in alkali darkening reactions to a similar extent as free hydroxide ions.

The formation of magnesium hydroxide under the alkaline conditions used in peroxide bleaching is clearly undesirable as it results in increased consumption of alkali and potentially leads to darkening of the pulp. However, magnesium hydroxide has also been reported to be virtually inactive as an inhibitor of cellulose degradation during oxygen bleaching of chemical pulps[229], implying that it cannot deactivate the transition metal ions present. Figures 5.21 and 5.22 show the effects of the addition of magnesium hydroxide, corresponding to the optimum level of magnesium determined in Figure 5.15, on the peroxide consumption during the bleaching of chelated and unchelated TMP respectively. Clearly the presence of magnesium hydroxide alone is not sufficient to account for the stabilization observed on the addition of magnesium nitrate, implying that magnesium hydroxide is not the main stabilizing species present during the bleaching reactions.

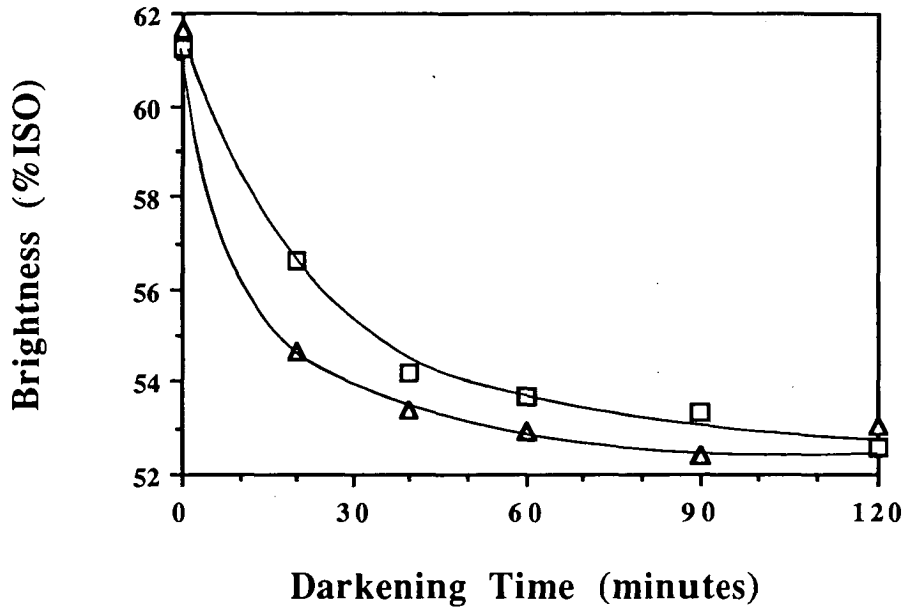

Figure 5.19 : Effects of (□) magnesium hydroxide and (△) sodium hydroxide on the darkening of chelated *P. radiata* TMP in the absence of peroxide. Alkali charge : $[OH^-] = 3.16 \times 10^{-2}$ M.

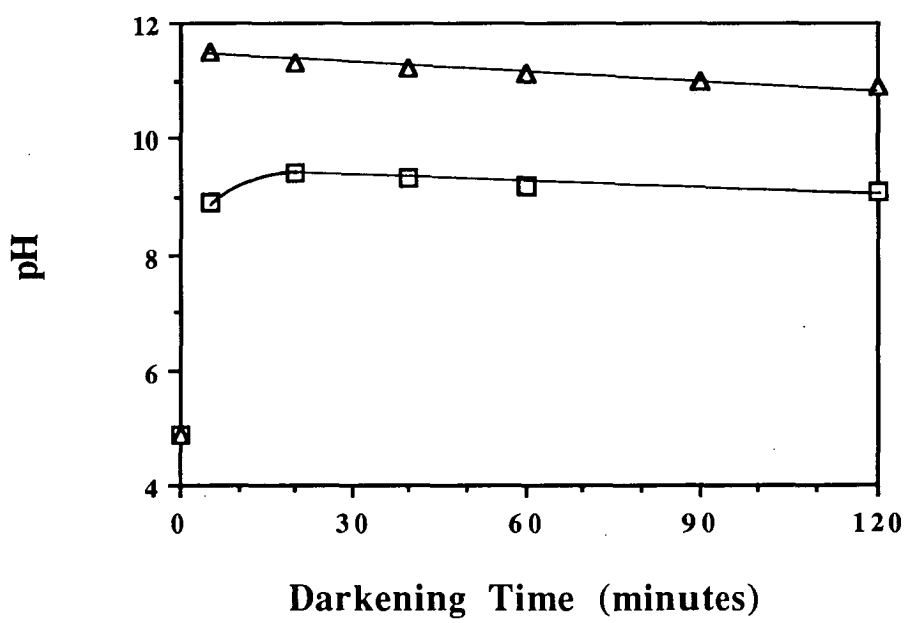

Figure 5.20 : Effects of (□) magnesium hydroxide and (△) sodium hydroxide on the pH during the darkening of chelated *P. radiata* TMP in the absence of peroxide. Alkali charge : $[OH^-] = 3.16 \times 10^{-2}$ M.

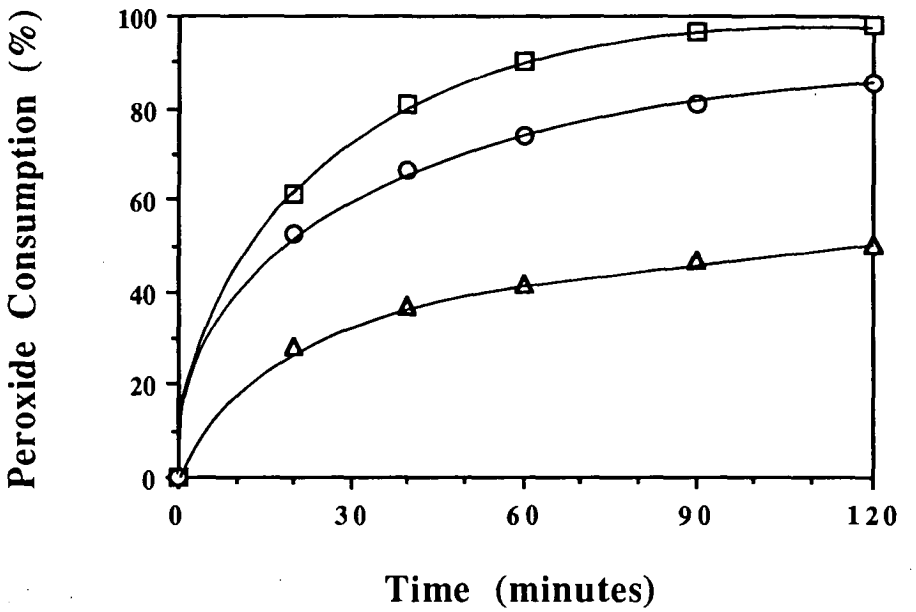

Figure 5.21 : Effect of magnesium source on peroxide consumption observed during bleaching *P. radiata* TMP. (□) no magnesium added : [Mg] = 2.4×10^{-3} M added as : (△) magnesium nitrate ; (○) magnesium hydroxide.

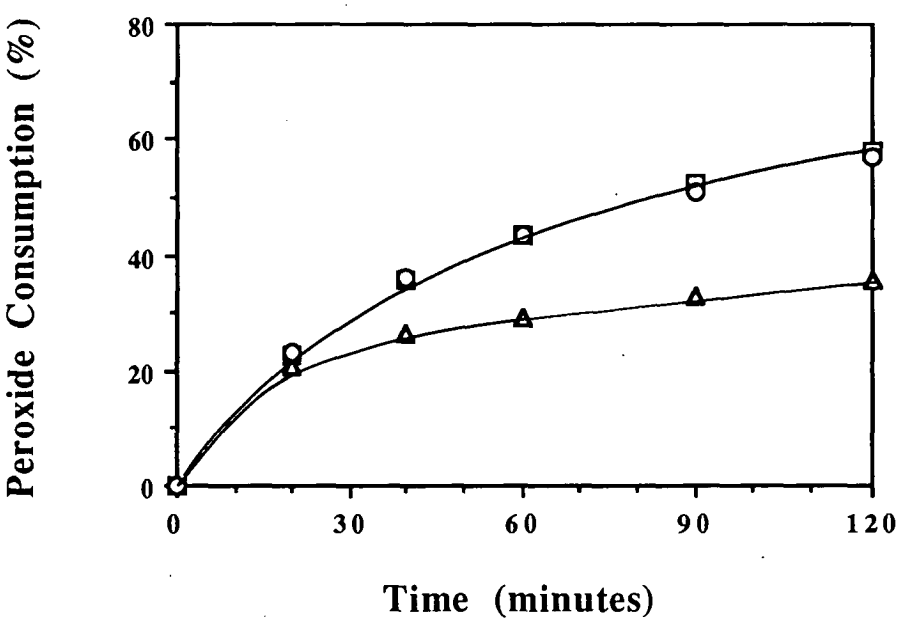

Figure 5.22 : Effect of magnesium source on peroxide consumption observed during bleaching chelated *P. radiata* TMP. (□) no magnesium added : [Mg] = 2.4×10^{-3} M added as : (△) magnesium nitrate ; (○) magnesium hydroxide.

5.6.4 Use of Soluble Magnesium Complexes as Peroxide Stabilizers During Bleaching

Soluble magnesium complexes have been reported to be highly efficient cellulose degradation inhibitors during oxygen bleaching reactions[115,228,229,233], with the level of addition required often less than the magnesium content of the wood itself[229]. While magnesium can be added in complexed form, it has also been suggested that magnesium can form complexes with organic acids which are generated during the reaction, with the resulting soluble species acting as inhibitors[115,228]. The formation of organic by-products, including acidic functionalities, as a result of peroxide bleaching of mechanical pulp is well established[158,226]. The interaction of such organic groups and magnesium might therefore be expected to result in the formation of soluble complexes during peroxide bleaching of mechanical pulps. Indeed, earlier studies have shown that a significant proportion of the magnesium added to the pulp was present in a soluble form during peroxide bleaching of TMP whereas, under identical conditions in the absence of pulp, virtually no magnesium was soluble (see section 3.2). The solubility of the magnesium during bleaching can therefore be directly attributed to interactions with organic components from the pulp itself. As magnesium hydroxide has been shown to be relatively inactive as a peroxide stabilizer, it seems likely that soluble complexes formed between the added magnesium and organic by-products of the bleaching reaction are predominantly responsible for the observed stabilizing effects.

While there are numerous reports in the literature dealing with various peroxide stabilizing agents, there appear to have been no studies into the use of magnesium complexes for this purpose. A recent study by Burton has shown that in the presence of sodium silicate the addition of small doses of magnesium sulfate can result in improved bleaching responses[28]. A study of the solubility of the additives revealed

that magnesium alone, which was inactive as a stabilizer, formed a precipitate in the bleach liquor whereas in the presence of silicate no precipitate was observed[28]. The presence of silicate appears to lead to the formation of a soluble or colloidal magnesium-silicate complex, with the complexed magnesium capable of exerting an influence on the stability of the peroxide and hence, on the bleaching response[9,18]. However, these results are complicated by the fact that silicate itself acts as a peroxide stabilizer.

Figures 5.23 and 5.24 show the effects of the addition of a soluble magnesium gluconate complex on the bleaching of TMP. The behaviour with respect to both peroxide consumption, Figure 5.23, and brightness gains, Figure 5.24, was found to be almost identical using the soluble magnesium complex and magnesium nitrate for low levels of addition. However, the negative effects attributed to the formation of magnesium hydroxide observed using high doses of magnesium nitrate are largely absent during bleaching with the soluble magnesium complex.

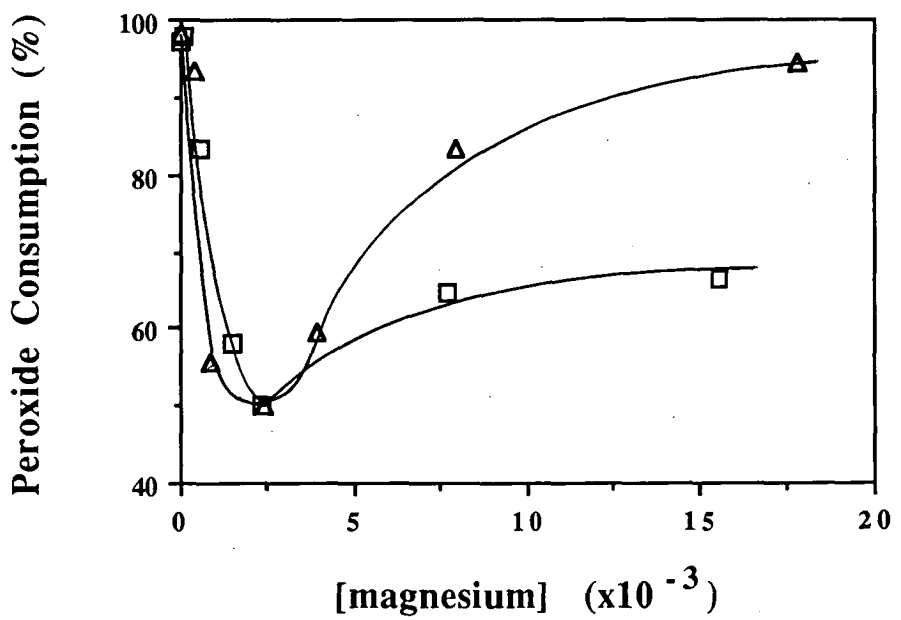

Figure 5.23 : Effects of the addition of magnesium gluconate (□) and magnesium nitrate (Δ) on peroxide consumption during the bleaching of TMP. (120 minutes).

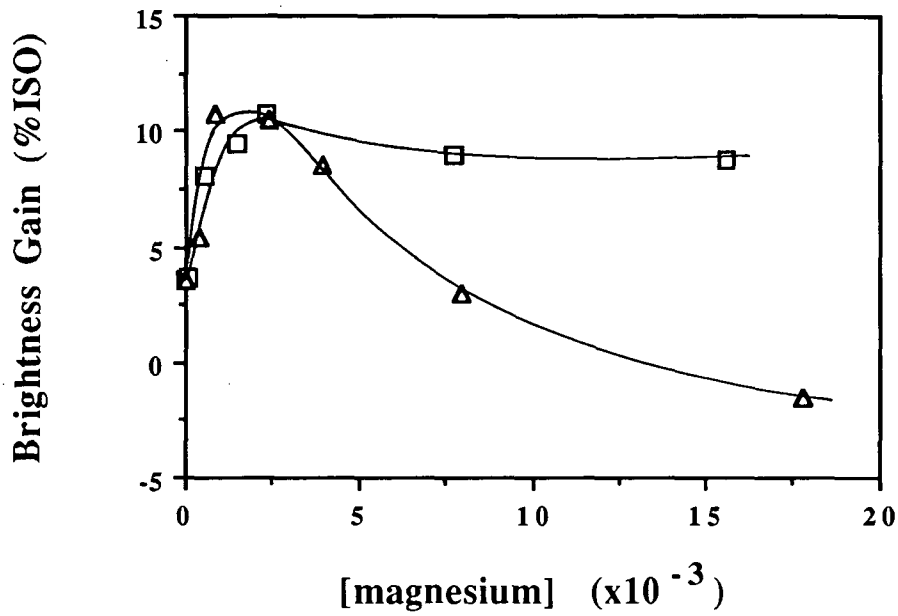

Figure 5.24 : Effects of the addition of magnesium gluconate (□) and magnesium nitrate (Δ) on brightness gains following the bleaching of TMP. (120 minutes).

5.6.5 Effects of Pulp Consistency on the Stabilization of Peroxide by Magnesium

The presence of the transition metals iron, copper and manganese has been shown to have little effect on the optimum level of magnesium nitrate required for peroxide stabilization during the bleaching of *P. radiata* TMP (section 5.6.2). A similar observation was made using sodium silicate as a peroxide stabilizer. A study of the effects of changing the pulp consistency demonstrated that the concentration of silicate in solution was the important factor in determining the level of stabilization (section 5.5.3). As the stabilizing ability of magnesium nitrate was found to stem from its ability to form complexes with various organic components from the pulp, it is possible that a more complicated relationship exists to define the optimum level of the additive. Therefore, in order to gain more information about the effects of magnesium during bleaching, a series of experiments was conducted to examine the influence of

pulp consistency on the stabilizing ability of the additive.

The experimental conditions employed were identical to those described earlier for sodium silicate (section 5.5.3), with constant pH conditions employed at 1 and 4% consistency, and variable pH conditions at 12% consistency. For each consistency studied the level of magnesium addition can be represented as either a concentration in solution or a percentage on pulp.

The effects of pulp consistency on stabilization by magnesium during the bleaching of *P. radiata* TMP are shown in Figures 5.25 and 5.26. The results suggest that unlike silicate, the optimum level of magnesium addition is not simply related to the concentration of magnesium in solution, Figure 5.25. The observed increase in the concentration of magnesium required for maximum stabilization as the pulp consistency was increased cannot be attributed to the effective increase in concentration of transition metals. However, the observed behaviour is consistent with the concept of complex formation between magnesium and various organic components of the pulp. Increasing the pulp consistency results in an increase in the concentration of the organic components present and hence, a potential increase in the concentration of the complexed magnesium species which are thought to be the active stabilizing agents. This is also reflected in the results presented in Figure 2.26 where the optimum level of magnesium, represented as a percentage on pulp, was similar for all the pulp consistencies studied.

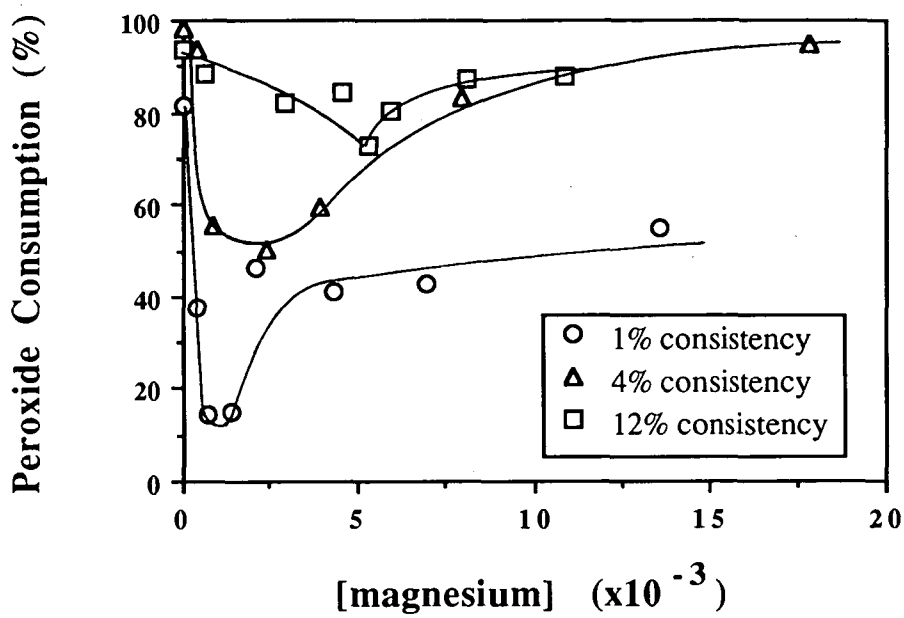

Figure 5.25 : Effect of pulp consistency on peroxide consumption during bleaching of *P. radiata* TMP in the presence of magnesium nitrate. Mg dose represented as a concentration in solution. Reaction time = 120 minutes.

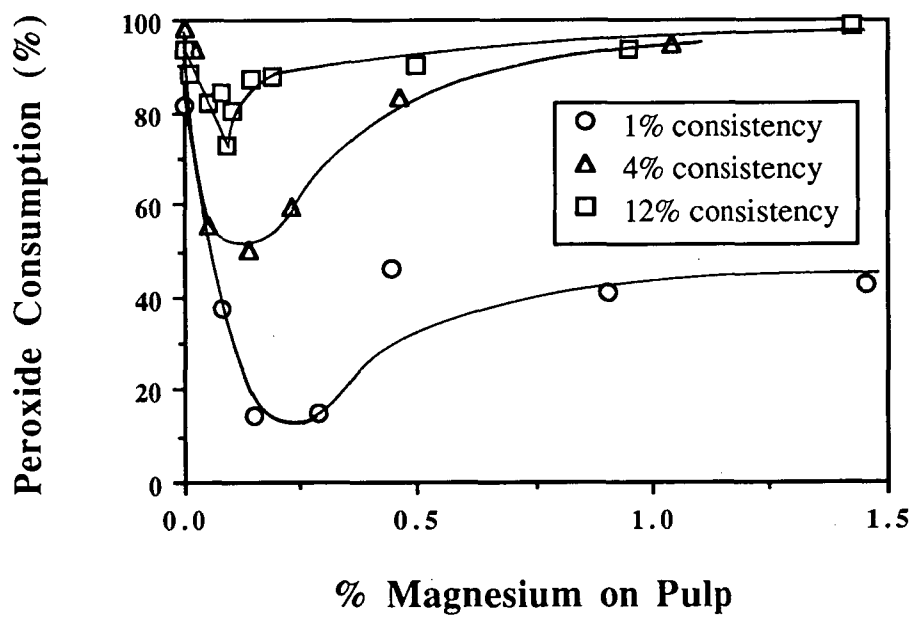

Figure 5.26 : Effect of pulp consistency on peroxide consumption during bleaching of *P. radiata* TMP in the presence of magnesium nitrate. Mg dose represented as a percentage on pulp. Reaction time = 120 minutes.

5.7 Comparison of Sodium Silicate and Magnesium as Peroxide Stabilizers During Bleaching

The effectiveness of sodium silicate as a stabilizer has resulted in its widespread use in the pulp and paper industry[23,31]. However, problems such as scaling and fouling of equipment have been associated with silicate use[12,16], and these factors may be significant, particularly if bleaching liquors are to be recycled[10]. It is therefore desirable to develop alternatives to silicate for use as stabilizers during peroxide bleaching reactions. The results presented in this study have demonstrated that magnesium salts can be successfully used as the sole stabilizer during the peroxide bleaching of mechanical pulps. The best results were obtained by adding the magnesium to the pulp prior to the addition of alkali or peroxide, thus minimizing the formation of insoluble magnesium hydroxide which is relatively inactive as a stabilizer. It is therefore of interest to compare the relative effects of sodium silicate and magnesium with respect to both the stabilization of peroxide and brightness response during bleaching.

Table 5.2 shows the levels of peroxide consumption and brightness gains achieved using the optimum doses of sodium silicate or magnesium nitrate during the bleaching of *P. radiata* TMP, both in the presence and absence of added transition metal ions. It should be noted that the optimum dose of magnesium was chosen with respect to the brightness gains achieved. While higher doses of magnesium can result in lower levels of peroxide consumption, the brightness gains obtained are lower, due to the negative effects associated with magnesium hydroxide formation. It is apparent from Table 5.2 that magnesium is capable of producing similar levels of peroxide stabilization to sodium silicate under the conditions of constant pH employed in the current study. However, the brightness gains obtained using sodium silicate were generally marginally higher than those found using magnesium as the sole stabilizer. It

seems likely that the increased brightness gains due to the increased availability of peroxide in bleaching systems stabilized by magnesium are partially offset by the darkening effects attributable to magnesium hydroxide formation, resulting in lower observed brightness gains in comparison to systems stabilized by sodium silicate.

Table 5.2 : Effects of optimum levels of sodium silicate or magnesium nitrate on the bleaching of *P. radiata* TMP. ($3.3x10^{-2}$ M silicate, $2.5x10^{-3}$ M magnesium, reaction time : 120 minutes).

Pulp Type	Peroxide Consumption (%)		Brightness Gain (%ISO)	
	magnesium	silicate	magnesium	silicate
TMP	50.2	47.7	10.1	10.8
Chelated TMP	35.4	38.7	10.5	11.3
Chelated + Fe	42.7	44.6	11.0	11.1
Chelated + Cu	66.1	62.6	7.9	8.1
Chelated + Mn	47.3	45.5	9.1	9.5

While it has been demonstrated that magnesium salts are capable of stabilizing peroxide during the bleaching of TMP, it is unlikely that their use would be feasible in industrial applications. The relatively high doses required, particularly at high consistencies, together with the undesirable effects of magnesium hydroxide formation, which include the consumption of alkali and alkali darkening, mean that sodium silicate will remain the preferred choice as an additive. However, the results obtained using a

soluble magnesium gluconate complex indicated that the negative effects associated with magnesium hydroxide formation can be minimized, suggesting that magnesium in the form of soluble complexes may provide viable alternatives to the use of sodium silicate as peroxide stabilizers during the bleaching of mechanical pulps.

5.8 Conclusions

The effects of the transition metals iron, copper and manganese, together with the additives sodium silicate and magnesium nitrate on the peroxide bleaching of *P. radiata* TMP have been examined. The major findings can be summarised as follows;

1) The negative effects associated with the naturally occurring transition metals present in the TMP were demonstrated by the reduction in peroxide consumption and increased brightness gains following chelation of the pulp with DTPA.

2) Manganese was found to be the predominant peroxide decomposition catalyst present in the *P. radiata* TMP used in the present study.

3) The addition of freshly prepared transition metals to chelated TMP resulted in increased peroxide consumption and corresponding decreased brightness gains.

4) The order of effectiveness of the added transition metal peroxide decomposition catalysts was found to be Fe > Mn > Cu.

5) The addition of sodium silicate resulted in decreased peroxide consumption and increased brightness gains when bleaching both TMP and chelated TMP.

6) The addition of sodium silicate resulted in decreased peroxide consumption and increased brightness gains when bleaching chelated TMP enriched with the transition metals iron, copper or manganese.

7) A similar optimum level of silicate addition was found irrespective of the presence or absence of the transition metals.

8) The concentration of silicate in solution is the primary factor in determining the stabilizing behaviour observed during peroxide bleaching. As a result, the percentage of silicate on pulp required for maximum stabilization decreases as the pulp consistency is increased.

9) The addition of magnesium was found to result in decreased peroxide consumption and increased brightness gains during the bleaching of TMP and chelated TMP.

10) The addition of higher than optimum doses of magnesium resulted in increased peroxide consumption in the presence of TMP, but had little effect on peroxide consumption in the presence of chelated TMP.

11) The addition of higher than optimum doses of magnesium resulted in decreased brightness gains for bleaching both TMP and chelated TMP.

12) The addition of magnesium was found to result in decreased peroxide consumption and increased brightness gains during the bleaching of chelated TMP enriched with iron, copper or manganese.

13) The addition of higher than optimum doses of magnesium resulted in increased peroxide consumption during the bleaching of chelated TMP in the presence of added manganese, but had little effect on peroxide consumption in the presence of added iron or copper.

14) The addition of higher than optimum doses of magnesium resulted in decreased brightness gains for the bleaching of enriched chelated TMP, irrespective of which transition metal was added.

15) The pulp darkening effect observed at high levels of magnesium addition can be attributed to the formation of magnesium hydroxide.

16) Hydroxide added as magnesium hydroxide appears to participate in alkali darkening reactions to a similar extent as hydroxide added in the form of sodium hydroxide, despite a large discrepancy in the measured pH values.

17) Magnesium hydroxide was not the predominant stabilizing species present during the bleaching reactions.

18) The active stabilizing agents were found to be soluble complexes formed between magnesium and various organic components derived from the pulp.

19) The addition of magnesium in the form of a soluble complex gave similar peroxide stabilization properties to those observed for the optimum dose of magnesium nitrate, while substantially reducing the negative effects associated with the formation of magnesium hydroxide.

20) Comparison of the effects of optimum levels of sodium silicate and magnesium nitrate revealed that similar levels of stabilization are obtained. However, the brightness gains observed in the presence of silicate were marginally superior to those observed with magnesium, due to the negative effects associated with the formation of magnesium hydroxide.

21) Soluble magnesium complexes may provide a viable alternative to sodium silicate as peroxide stabilizers during the bleaching of mechanical pulp.

CHAPTER 6

Summary and Conclusions

6.1 Summary and Conclusions

The present study has investigated various aspects of the peroxide decomposition behaviour in the presence of transition metal ions under the alkaline conditions which are typically encountered during the peroxide bleaching of mechanical pulps. A particular emphasis has been placed on the elucidation of the mechanisms involved during the stabilization or acceleration of the rate of metal catalysed peroxide decomposition by various additives, both in the presence and absence of pulp. In addition, the effects of the common peroxide stabilizers sodium silicate and magnesium on the bleaching of a mechanical pulp have been examined in the presence and absence of added transition metal ions.

The catalytic behaviour of transition metals towards peroxide decomposition under alkaline conditions has been shown to be closely related to the hydrolysis species present. The decreased rates of peroxide decomposition observed on the aging of iron and copper can be attributed to the formation of less catalytically active hydrolysis species of these metals with time. In the presence of various additives, which were also capable of undergoing hydrolysis reactions under alkaline conditions, a correlation was observed between the catalytic activity of the transition metals and the formation of transition metal-additive complexes, which could be monitored by UV-visible spectroscopy. This finding led to the conclusion that the observed rates of catalytic peroxide decomposition depends on the actual species present, with the species probably containing structural units of the type M_1-O-M_2, where M_1 = Fe, Cu, Mn and M_2 = Si, Mg, Al, Zn. Importantly, the formation of complexes of this type can account for both the stabilization and acceleration of rates of peroxide decomposition observed with different combinations of transition metals and additives.

A study of the solubility of transition metal species under alkaline conditions

demonstrated that the inclusion of the additives sodium silicate or magnesium can have a considerable influence on the behaviour of the species, providing further evidence supporting the concept of direct interactions between the metals and additives. An extension of this study also identified that the inclusion of pulp was capable of having a significant effect on the solubility behaviour observed, leading to the possibility that the catalytic behaviour may be significantly modified in the presence of pulp.

A series of experiments conducted under identical conditions of temperature and pH revealed that, for certain systems of transition metals and additives, the catalytic behaviour towards peroxide decomposition was indeed dependent on the presence or absence of pulp. In these cases, it was found that the variations in peroxide decomposition behaviour observed on the inclusion of pulp could be simulated by the addition of model compounds representing various components expected to be present in systems containing pulp. These results demonstrate the inherent dangers associated with predicting the behaviour of peroxide stabilizing agents during bleaching reactions, based on the results of studies conducted in the absence of pulp.

In addition to the examination of their effects on peroxide decomposition rates, the effects of the stabilizers sodium silicate and magnesium on bleaching responses were also examined. Sodium silicate proved to be an effective stabilizing agent, both in the presence and absence of added transition metal ions, with decreases in peroxide consumption being associated with increased brightness gains. It was also demonstrated that the concentration of sodium silicate in solution was the primary factor involved in determining the stabilizing behaviour during peroxide bleaching. Like sodium silicate, magnesium was found to be an effective stabilizing agent during bleaching, with its addition capable of producing increased brightness gains together with decreased peroxide consumption. However, the addition of excess magnesium was found to result in the darkening of the pulp, which can be attributed to alkali

darkening reactions involving precipitated magnesium hydroxide. The stabilizing action of magnesium was found to involve the formation of soluble magnesium species, presumably through interactions with soluble components from the pulp. It was demonstrated that the addition of magnesium in the form of a soluble complex produced an effective stabilizing system, minimizing the negative effects associated the the formation of magnesium hydroxide.

CHAPTER 7

Experimental

7.1 Reagents

Two samples of A.R. grade hydrogen peroxide, A (from BDH Chemicals) and B (from Ajax chemicals), were employed in the current study. Sample A was used in the peroxide decomposition experiments conducted at 20°C reported in Chapter 2, while the remaining studies, conducted at 50°C, employed sample B. Trace metal analysis using atomic absorption was carried out by the CSIRO Marine Laboratories in Hobart, Tasmania, to determine the purity of the peroxide samples, and the results are shown in Table 7.1. Levels of metallic impurities are comparable to other reported analyses[234]. Results of analysis of Milli-Q deionised water, which was used throughout the current study, are also given.

Many previous investigations have noted the importance of the purification of alkali as this is usually a major source of the metallic impurities which lead to decomposition in alkaline peroxide solutions[47,50]. The current study employed semiconductor grades of sodium and potassium hydroxide (99.99%) which were obtained from Aldrich Chemicals. These samples contain very low levels of trace metal impurities, as shown by the manufacturers analysis for the potassium hydroxide in Table 7.1, and are ideally suited to the investigation of peroxide decomposition behaviour. Potassium hydroxide was employed in the studies reported in Chapter 2, while sodium hydroxide was utilized in all remaining experiments.

The transition metal used in the current study were iron (III) nitrate (99.99+%), copper nitrate (99.999%) and manganese nitrate (99.99%), all of which were supplied by Aldrich Chemicals.

Chemicals employed as additives in the present study were magnesium nitrate (99.999%), sodium silicate (30% SiO_2), magnesium hydroxide (95%) and magnesium

gluconate (97%) which were supplied by Aldrich Chemicals, aluminium nitrate (98.0%) and sodium nitrate (99.0%) obtained from Ajax Chemicals, and zinc nitrate (96+%) supplied by BDH Chemicals. The chelating agent DTPA (97%) was obtained from Aldrich Chemicals.

Table 7.1 Trace metal analysis of some chemicals used in this study.

Metal	Milli-Q (mg/L)	Peroxide A (mg/L)	Peroxide B (mg/L)	KOH (mg/kg)
Ag	-	-	-	7
Ca	-	-	-	0.9
Cd	0.00	0.15	0.12	-
Co	0.7	0.6	1.1	-
Cr	0.2	2.6	1.3	-
Cu	0.2	3.3	0.9	-
Fe	0.4	9.8	1.8	0.7
Mg	-	-	-	0.08
Mn	0.2	1.0	1.0	0.7
Na	-	-	-	250
Ni	0.3	4.0	4.8	-
Pb	0.0	2.8	2.6	-
Zn	0.6	5.5	6.5	3

The model compounds employed in the studies described in Chapter 4 were cinnamic acid (99+%), 3,4-dimethoxycinnamic acid (99%), 4-hydroxy-3-methoxybenzoic acid (97%), 3,4-dimethoxybenzoic acid (99+%), 3,4,5-trimethoxyacetophenone (98%), acetovanillone (98%), vanillin (99%), gluconic acid (45-50 wt % aqueous solution), glucuronic acid (99%), adipic acid (99%) and oxalic acid (98%) which were obtained from Aldrich Chemicals. Acetic acid (A.R. grade) was obtained from BDH chemicals,

while formic acid (A.R. grade) was obtained from Ajax Chemicals.

All chemicals employed in the current study were found to be of a sufficiently high purity to allow their use without further purification.

7.2 Pulp Samples

Pinus radiata thermo-mechanical pulp (TMP) was provided by Australian Newsprint Mills, Boyer Mill, and stored at 8% consistency and 4°C until used. Chelated pulp was prepared by addition of 0.5% DTPA to the TMP (2% consistency) at 20°C followed by stirring for ~30 minutes. The resulting pulp was filtered and washed thoroughly with Milli-Q deionised water.

Bleached *Pinus radiata* kraft pulp was obtained from Tasman Pulp and Paper, New Zealand. The pulp was slurried and prebleached with hydrogen peroxide (initial conditions : 7.5% peroxide on pulp, pH 11, 50°C, 4% consistency, 60 minutes) followed by filtration and thorough washing with Milli-Q deionised water prior to use.

7.3 Procedures Employed in Peroxide Decomposition Studies

The following procedures were employed unless stated in the text.

7.3.1 Hydrogen Peroxide Determination

The extent of reactions involving hydrogen peroxide was monitored by titrimetric determination of 5.0ml samples withdrawn at intervals. Samples were acidified with sulphuric acid, and excess potassium iodide added together with a few drops of

ammonium molybdate solution. The liberated iodine was titrated against standardized sodium thiosulfate solution[235,236].

7.3.2 UV-visible Spectroscopy

UV-visible spectra were recorded using a Varian DMS 100 spectrophotometer. The measurement of the spectra of solutions containing iron was carried out prior to the addition of hydrogen peroxide. In experiments containing added copper the UV-visible spectra were recorded 30 minutes after peroxide addition.

7.3.3 Solubility Measurements During Solution Studies

Samples of liquors from peroxide decomposition experiments were withdrawn at regular intervals and filtered with a 0.45 μm syringe filter, obtained from Millipore, with the resulting solution used for analysis of soluble transition metals and additives. The levels of metal ions and additives in these solutions were determined by atomic absorption using a Varian spectrAA-10 spectrophotometer.

7.3.4 Peroxide Decomposition Experiments

All peroxide decomposition experiments were carried out in polyethylene bottles supported in a constant temperature bath. The bottles were cleaned between experiments using warm dilute sulphuric acid and rinsed thoroughly with Milli-Q deionised water to prevent the accumulation of metal ion impurities. Mechanical stirring was provided ensuring that only plastic material was in contact with the solutions.

It has previously been suggested that the decomposition of alkaline hydrogen peroxide can take place through heterogeneous catalytic processes on the surface of the reaction

vessel[49,50]. The present study found that no significant increase in reaction rate could be detected at either pH 9 or 11 by introducing additional surface area in the form of parts of a polyethylene reaction vessel placed into the solution, increasing the available surface area by a factor of ~3. These observations suggest that the reported effects due to heterogeneous reactions at the vessel walls are probably due to leaching of metal ions under alkaline conditions, particularly when glass vessels are used.

7.3.4.1 Peroxide Decomposition at 20°C : Chapter 2

Decomposition experiments were carried out in hydrogen peroxide solutions with initial concentration 0.10M prepared by addition of 5.0ml of concentrated hydrogen peroxide to an appropriate volume of Milli-Q water, to which the desired metal nitrate, additive and appropriate level of potassium hydroxide had been added. The total volume of solution used was 500ml. The initial concentration of iron nitrate introduced was 1.98×10^{-4} M in all experiments, while the level of copper nitrate added was 2.14×10^{-4} M in all cases.

7.3.4.2 Peroxide Decomposition at 50°C : Chapter 4

Peroxide decomposition experiments conducted at 50°C used an initial peroxide concentration of 0.035 M and a total volume of 500mls. The desired transition metal ions and additives were added 5 minutes prior to the peroxide in all cases. An initial charge of sodium hydroxide was added 30 seconds prior to the peroxide, with the pH adjusted to 11.0 immediately following its addition. The pH was maintained at 11.0 throughout the course of the reactions by the addition of sodium hydroxide or sulphuric acid as required.

7.3.5 Peroxide Decomposition Experiments in the Presence of Model Compounds

The peroxide decomposition experiments in the presence of model compounds reported in Chapter 4 were conducted in an identical manner to conventional peroxide decomposition experiments (see section 7.3.4.2). Model compounds were added 10 minutes prior to peroxide, ie. 5 minutes prior to the metal ions and additives, in each case. The concentrations of model compounds used was 3.6×10^{-3} M, unless stated in the text.

7.3.6 Peroxide Decomposition Experiments in the Presence of Bleached Kraft Pulp

Peroxide decomposition experiments conducted in the presence of bleached kraft pulp (4% consistency) were performed under identical conditions to those employed in the solution study (see section 7.3.4.2). The level of peroxide decomposition was determined following filtration to remove the pulp fibres.

7.4 Procedures Employed During Peroxide Bleaching Studies

The following procedures were employed unless stated in the text.

7.4.1 Determination of Hydrogen Peroxide Residuals

Pulp samples were withdrawn at regular time intervals and filtered to remove pulp fibres. The peroxide content of a 5ml aliquot of the filtrate was then determined by the procedure described above (section 7.3.1).

7.4.2 Measurement of Pulp Brightness

Pulp samples (~5g o.d.) were withdrawn at regular intervals, filtered and washed with ~100mls Milli-Q deionised water. The filtered pulp was then re-suspended in ~200mls Milli-Q water. Brightness pads were then formed by filtering the pulp suspension using a Whatman Number 1 filter paper. The pad was washed once more with ~100mls Milli-Q water prior to drying at room temperature. The brightnesses of the resulting handsheets were measured using an Elrepho 2000 using a 457nm filter.

7.4.3 Determination of Metal Contents of Pulps

The pulp to be analysed (~10g o.d.) was placed in pre-weighed 500ml conical boiling flasks and placed in an oven at ~120°C overnight to allow the o.d. weight to be accurately determined. The pulps were then digested using the following procedure. 50mls of concentrated nitric acid and 5 mls of concentrated sulphuric acid were added, and the flasks were gently heated. Following an initial vigorous reaction the flasks were heated further until no pulp remained visible. 5mls of perchloric acid (70%) was then added and the solutions boiled until a clear straw colour was obtained. After cooling the solutions were accurately diluted to 100mls using Milli-Q deionised water, and the metal contents were determined by atomic adsorption using a Varian spectrAA-10 spectrophotometer. The metal ion contents of the pulp are reported in the text where appropriate.

7.4.4 Solubility Measurements During Bleaching Studies

Samples of pulp slurries to be analysed were withdrawn and filtered using a Whatman No. 1 filter paper. The concentrations of metal ions and additives in the filtrate were then determined as described in section 7.3.3, again after filtration with a 0.45 μm syringe filter.

7.4.5 Peroxide Bleaching Experiments

Bleaching experiments were carried out at 50°C and pH 11.0 (constant) in polyethylene reaction vessels using a pulp consistency of 4%, initial peroxide concentration of 0.035M (3% on o.d. pulp) and total volume of 500 mls, unless stated. Transition metal and additives were added 5 minutes prior to the peroxide where appropriate. An initial charge of sodium hydroxide was added 30 seconds prior to the peroxide, with the pH adjusted to 11.0 immediately following its addition. The pH was maintained at 11.0 by the addition of sodium hydroxide or sulphuric acid as required. Pulp suspensions were stirred during the course of the bleaching reactions and samples withdrawn at regular intervals for analysis.

7.4.5.1 Bleaching Under Constant Conditions

Constant conditions bleaching was conducted at 50°C, pH 11.0 (constant) at a pulp consistency of 4%. In order to maintain a constant level of peroxide during constant conditions bleaching, a number of preliminary bleaching reactions were conducted to determine the initial rate of peroxide consumption. The desired amount of peroxide was then added to the bleaching mixture at regular time intervals (2.5-5 minutes) to maintain the initial peroxide charge over the course of the reaction. The pH was maintained at a constant level by the addition of sodium hydroxide or sulphuric acid as required.

7.4.5.2 Bleaching at Variable Consistencies

Additional bleaching experiments were conducted at 1% consistency (50°C, pH 11.0 (constant), initial peroxide concentration 0.035M, total volume 500 mls) and 12% consistency (50°C, initial pH 11.0 (variable), initial peroxide concentration 0.120M,

total volume 73 mls).

7.4.6 Alkali Darkening Experiments

Alkali darkening experiments were carried out at 50°C using a pulp consistency of 4%. The brightness (% ISO) of the bleached and darkened pulps were measured using an Elrepho 2000 with a 457 nm filter.

CHAPTER 8

References

1. Smook, G.A., *J. Chem. Tech. Biotechnol.*, 45, 15 (1989).
2. Hart, J.R., *Pulp Paper*, 55(6), 138 (1981).
3. Pearson, J., *Pulp Paper Int.*, 34(3), 50 (1992).
4. Reichert, J.S. and Pete, R.H., *Tappi*, 32(3), 97 (1949).
5. Lachenal, D., de Choudens, C. and Monzie, P., *Tappi*, 63(4), 119 (1980).
6. Lachenal, D., Soria, L., de Choudens, C. and Monzie, P.,Tappi Int. Pulp Bleach. Conf., 145 (1982).
7. Hartler, N., Lindahl, E., Moberg, C.G. and Stockman, L., *Tappi*, 43(10), 806 (1960).
8. McDonough, T.J., *Pulp Paper Can.*, 93(4), T108 (1992).
9. Andrews, D.H., *Pulp Paper Mag. Can.*, 69(11), T273 (1968).
10. Kindron, R.R., *Pulp Paper*, 54(11), 127 (1980).
11. Gupta, V.N. and Mutton, D.B., *Pulp Paper Mag. Can.*, 70(6), 77 (1969).
12. Slove, M.L., *Tappi*, 48(9), 535 (1965).
13. Teder, A. and Tormund, D., *Svensk Papperstidn.*, 83(4), 106 (1980).
14. Mulcahy, J.P., Neilson, M.J. and Maddern, K.N., *Appita*, 42(6), 424 (1989).
15. Strunk, W.G., *Pulp Paper*, 54(6), 156 (1980).
16. Strunk, W.G. and Meng, T., *Pulp Paper*, 54(6), 156 (1980).
17. Thiessen, F.I., *Pulp Paper*, 53(1), 161 (1979).
18. Dick, R.H. and Andrews, D.H., *Pulp Paper Mag. Can.*, 66(3), T201 (1965).
19. Reichert, J.S., Campbell, D.J. and Mills, R.T., *Paper Trade J.*, 118(15), 125 (1944).
20. Read, D.W., Eade, B.D. and Slingsby, N.R., *Pulp Paper Mag. Can.*, 69(13), T296 (1968).
21. Burton, J.T. and Campbell, L.L., Int. Symp. Wood Pulping Chem., 255 (1985).
22. Colodette, J.L. and Dence, C.W., *J. Pulp Paper Sci.*, 15(3), J79 (1989).
23. Dence, C.W. and Omori, S., *Tappi*, 71(10), 120 (1986).

24. Nicoll, W.D. and Smith, A.F., *Ind. Eng. Chem.*, 47(12), 2548 (1955).

25. Colodette, J.L., Rothenberg, S. and Dence, C.W., *J. Pulp Paper Sci.*, 15(1), J3 (1989).

26. Colodette, J.L., Rothenberg, S. and Dence, C.W., *J. Pulp Paper Sci.*, 15(2), J45 (1989).

27. Abbot, J., *J. Pulp Paper Sci.*, 17(1), J10 (1991).

28. Burton, J.T., *J. Pulp Paper Sci.*, 12(4), J95 (1986).

29. Bambrick, D.R., *Tappi*, 68(6), 96 (1985).

30. Kutney, G.W., *Pulp Paper Can.*, 86(12), T402 (1985).

31. Burton, J.T., Campbell, L.L. and Donnini, G.P., *Pulp Paper Can.*, 88(6), T224 (1987).

32. Melnyk, A.C., Kildahl, N.K., Rendina, A.R. and Busch, D.H., *J. Amer. Chem. Soc.*, 101(12), 3232 (1979).

33. Walling, C., *Acc. Chem. Res.*, 8, 125 (1975).

34. Kohler, J.T., Altomare, R.E. and Kittrell, J.R., *Ind. Eng. Chem., Prod. Res. Dev.*, 14(1), 36 (1975).

35. Razouk, R.I., Habashy, G.M. and Kelada, N.P., *J. Catal.*, 25, 183 (1972).

36. Lin, C.C., Smith, F.R., Ichikawa, N., Baba, T. and Itow, M., *Int. J. Chem. Kinet.*, 23, 971 (1991).

37. Sigel, H., *Angew. Chem., Int. Edit.*, 8(3), 167 (1969).

38. Mochida, I., Yasutake, A., Fujitsu, H. and Takeshita, K., *J. Phys. Chem.*, 86, 3468 (1982).

39. Sigel, H., Wyss, K., Fischer, B.E. and Prijs, B., *Inorg. Chem.*, 18(5), 1354 (1979).

40. Schubert, J., Sharma, V.S., White, E.R. and Bergelson, L.S., *J. Amer. Chem. Soc.*, 90(16), 4476 (1968).

41. Sharma, V.S. and Schubert, J., *Inorg. Chem.*, 10(2), 251 (1971).

42. Khangulov, S.V., Andreeva, N.E., Gerasimenko, V.V., Goldfeld, M.G., Barynin, V.V. and Grebenko, A.I., *Russ. J. Phys. Chem.*, 64(1), 10 (1990).

43. Fenton, H.J.H., *J. Chem. Soc.*, 65, 899 (1894).

44. Hiskey, J.B., *Trans. Inst. Min. Metall.*, 89, C145 (1980).

45. Duke, F.R. and Haas, T.W., *J. Phys. Chem.*, 65, 304 (1961).

46. Herbst, J.H.E. and Barton, S.C., *Tappi*, 46(8), 486 (1963).

47. Csanyi, L.J., Nagy, L., Galbacs, Z.M. and Horvath, L., *Z. Phys. Chem., Neue Folge*, 138, 107 (1983).

48. Csanyi, L.J., Galbacs, Z.M. and Horvath, L., *Inorg. Chim. Acta*, 55, 1 (1981).

49. Galbacs, Z.M. and Csanyi, L.J., *J. Chem. Soc., Dalton Trans.*, 2353 (1983).

50. Spalek, O., Balej, J. and Paseka, I., *J. Chem. Soc., Faraday Trans. 1*, 78, 2349 (1982).

51. Koubek, E., Haggett, M.L., Battaglia, C.J., Ibne-Rasa, K.M., Pyun, H.Y. and Edwards, J.O., *J. Amer. Chem. Soc.*, 85, 2263 (1963).

52. Evans, D.F. and Upton, M.W., *J. Chem. Soc., Dalton Trans.*, 2525 (1985).

53. Colodette, J.L., Rothenberg, S. and Dence, C.W., *J. Pulp Paper Sci.*, 14(6), J126 (1988).

54. Spitz, R.D., *Tappi*, 44(10), 731 (1961).

55. McKee, D.W., *J. Catal.*, 14, 355 (1969).

56. Ono, Y., Matsumura, T., Kitajima, N. and Fukuzumi, S., *J. Phys. Chem.*, 81(13), 1307 (1977).

57. Mochida, I. and Takeshita, K., *J. Phys. Chem.*, 78(16), 1653 (1974).

58. Maggs, F.T. and Sutton, D., *Trans. Faraday Soc.*, 55, 974 (1959).

59. Csanyi, L.J., Galbacs, Z.M. and Nagy, L., *J. Chem. Soc., Dalton Trans.*, 237 (1982).

60. Nagy, L., Galbacs, Z.M., Csanyi, L.J. and Horvath, L., *J. Chem. Soc., Dalton Trans.*, 859 (1982).

61. Goldstein, J.R. and Tseung, A.C.C., *J. Catal.*, 32, 452 (1974).

62. Ram, R.N. and Prasad, B.B., *Z. Phys. Chem., Leipzig*, 259(6), 1169 (1978).

63. Baxendale, J.H., *Adv. Catal.*, 4, 31 (1952).

64. Haber, F. and Weiss, J., *Proc. Royal Soc. A*, 147, 332 (1934).

65. Barb, W.G., Baxendale, J.H., George, P. and Hargrave, K.R., *Trans. Faraday Soc.*, 47, 462 (1951).

66. Barb, W.G., Baxendale, J.H., George, P. and Hargrave, K.R., *Trans. Faraday Soc.*, 47, 591 (1951).

67. Berdnikov, V.M., *Russ. J. Phys. Chem.*, 47(7), 1060 (1973).

68. Glasner, A., *J. Chem. Soc.*, 904 (1951).

69. Luo, Y., Kustin, K. and Epstein, I.R., *Inorg. Chem.*, 27, 2489 (1988).

70. Ahuja, L.D., Rajeshwer, D. and Nagpal, K.C., *J. Colloid Int. Sci.*, 119(2), 481 (1987).

71. Ahuja, L.D., Rajeshwer, D. and Nagpal, K.C., *J. Colloid Int. Sci.*, 123(2), 380 (1988).

72. Kanungo, S.B., Parida, K.M. and Sant, B.R., *Electrochim. Acta*, 26, 1157 (1981).

73. Sharma, V.S., Schubert, J., Brooks, H.B. and Sicilio, F., *J. Amer. Chem. Soc.*, 92(4), 822 (1970).

74. Sigel, H. and Muller, U., *Helv. Chim. Acta*, 49, 671 (1966).

75. Erlenmeyer, H., Muller, U. and Sigel, H., *Helv. Chim. Acta*, 49, 681 (1966).

76. Roy, C.B., *J. Catal.*, 12, 129 (1968).

77. Youssef, N.A., Selim, M.M. and Kamel, E.S., *Bull. Soc. Chim. Fr.*, 128, 648 (1991).

78. Mousa, M.A., *Proc. Pak. Acad. Sci.*, 24(4), 327 (1987).

79. Mooi, J. and Selwood, P.W., *J. Amer. Chem. Soc.*, 74, 1750 (1952).

80. Kitajima, N., Fukuzumi, S. and Ono, Y., *J. Phys. Chem.*, 82(13), 1505 (1978).

81. Jaiswal, D.K., Ram, R.N. and Prasad, B.B., *Z. Phys. Chem., Leipzig*, 263, 74 (1982).

82. Wang, J.H., *J. Amer. Chem. Soc.*, 59, 4715 (1955).

83. Kremer, M.L., *Int. J. Chem. Kinet.*, 17, 1299 (1985).

84. Kremer, M.L. and Stein, G., *Trans. Faraday Soc.*, 55, 959 (1959).

85. Isbell, H.S., Parks, E.W. and Naves, R.G., *Carbohydrate Res.*, 45, 197 (1975).

86. Francis, K.C., Cummins, D. and Oakes, J., *J. Chem. Soc., Dalton Trans.*, 493 (1985).

87. Walling, C., Kurz, M. and Schugar, H.J., *Inorg. Chem.*, 9(4), 931 (1970).

88. Aldridge, J. and Applebey, M.P., *J. Chem. Soc.*, 121, 238 (1922).

89. Wieland, H. and Stein, E., *Z. Anorg. Chem.*, 236, 361 (1938).

90. Hobbs, G.C. and Abbot, J., *J. Wood Chem. Technol.*, (submitted 1993).

91. Vierke, G., *Z. Naturforsch., Teil B*, 29(1-2), 135 (1974).

92. Ernestova, L.S., Skurlatov, Y.I. and Fursina, L.A., *Russ. J. Phys. Chem.*, 58(4), 554 (1984).

93. Ernestova, L.S. and Skurlatov, Y.I., *Russ. J. Phys. Chem.*, 58(9), 1436 (1984).

94. Ernestova, L.S. and Skurlatov, Y.I., *Russ. J. Phys. Chem.*, 58(3), 446 (1984).

95. Chouaib, F., Heubel, P.-H., Sanson, M.D.C., Picard, G. and Tremillon, B., *J. Electroanal. Chem.*, 127, 179 (1981).

96. Kutney, G.W. and Evans, T.D., *Svensk Papperstidn.*, 88(9), R84 (1985).

97. Broughton, D.B. and Wentworth, R.L., *J. Amer. Chem. Soc.*, 69, 741 (1947).

98. Broughton, D.B., Wentworth, R.L. and Laing, M.E., *J. Amer. Chem. Soc.*, 69, 744 (1947).

99. Kanungo, S.B., *J. Catal.*, 58, 419 (1979).

100. Abd El-Salam, K.M., *Z. Phys. Chem. Neue Folge*, 95, 139 (1975).

101. Baral, S., Lume-Pereira, C., Janata, E. and Henglein, A., *J. Phys. Chem.*, 89, 5779 (1985).

102. Agnemo, R., Gellerstedt, G. and Lindfors, E.-L., *Acta Chem. Scand.*, B33(2), 154 (1979).

103. Isbell, H.S., Frush, H.L. and Parks, E.W., *Carbohydrate Res.*, 51, C5 (1976).

104. Sychev, A.Y., Isak, V.G. and Lap, D.V., *Russ. J. Phys. Chem.*, 52(1), 55 (1978).

105. Whiting, P., Pitcher, J.M. and Manchester, D.F., *J. Pulp Paper Sci.*, 10(5), J119 (1984).

106. Basciano, C.R. and Heimberger, S.A., Tappi Pulping Conf., Book 2, 657 (1989).

107. Ali, T., McArthur, D., Stott, D., Fairbank, M. and Whiting, P., *J. Pulp Paper Sci.*, 12(6), J166 (1986).

108. Blasschette, A. Von. and Saad, S.M., *Holzforschung*, 23(5), 163 (1969).

109. Kanter, M.Y., Raskina, I.K., Bogdanov, G.A. and Kozlov, Y.N., *Zh. Prikl. Khim.*, 50, 724 (1977).

110. Sjostrom, E. and Valtilla, O., *Paperi ja Puu*, 60(1), 37 (1978).

111. Ericsson, B., Lindgren, B.O. and Theander, O., *Svensk Papperstidn.*, 74(22), 757 (1971).

112. Samuelson, O. and Stolpe, L., *Svensk Papperstidn.*, 72(20), 662 (1969).

113. Isbell, H.S. and Frush, H.L., *Carbohydrate Res.*, 59, C25 (1977).

114. Sinkey, J.D. and Thompson, N.S., *Paperi ja Puu*, 56(5), 473 (1974).

115. Gilbert, A.F., Pavlovova, E. and Rapson, W.H., *Tappi*, 56(6), 95 (1973).

116. Sjostrom, E. and Valtilla, O., *Paperi ja Puu*, 54(11), 695 (1972).

117. Moldenius, S., *J. Pulp Paper Sci.*, 10(11), J172 (1984).

118. Reichert, J.S., *Paper Trade J.*, 118(11), 89 (1944).

119. Paasonen, P.K., *Paperi ja Puu*, 52(9), 555 (1970).

120. Allison, R.W., *Appita*, 36(5), 362 (1983).

121. Fiala, W., Falk, B. and Ryrberg, G., *Das Papier*, 37(10A), V39 (1983).

122. Williams, M.D. and Garland, C.P., *Appita*, 41(2), 138 (1988).

123. Ariadi, B. and Abbot, J., *Appita*, 45(3), 178 (1992).

124. Gupta, M.K., *Tappi*, 59(11), 114 (1976).

125. Douek, M. and Goring, D.A.I., *Wood Sci. Technol.*, 10(1), 29 (1976).

126. Loras, V., *Tappi*, 59(11), 99 (1976).

127. Rothenberg, S. and Robinson, D.H., *Tappi*, 63(9), 117 (1980),

128. Abbot, J., Vanderaa, S., Ritz, A., Wright, P.J. and Ault, K., *Appita*, 45(6), 393 (1992).

129. McEwen, R.L., *Tech. Assoc. Papers*, 29, 278 (1945).

130. Meyrant, P. and Dodson, M., Tappi Pulping Conf., 669 (1989).

131. Moldenius, S., *Svensk Papperstidn.*, 85(15), R116 (1982).

132. Hobbs, G.C. and Abbot, J., *Appita*, 45(5), 344 (1992).

133. Moldenius, S. and Sjogren, B., *J. Wood Chem. Tech.*, 2(4), 447 (1982).

134. Hagglund, T. and Lindstrom, L., Int. Pulp Bleach. Conf., 163 (1985).

135. Liebergott, N., Van Lierop, B. and Heitner, C., Int. Mech. Pulp. Conf., 75 (1987).

136. Lachenal, D., Dubreuil, M. and Bourson, L., *Tappi*, 76(10), 195 (1990).

137. Martin, D.M., *Tappi*, 40(2), 65 (1957).

138. Martin, D.M., *Tappi*, 40(2), 72 (1957).

139. Colodette, J.L., Fairbank, M.G. and Whiting, P., *J. Pulp Paper Sci.*, 16(2), J53 (1990).

140 Kutney, G.W. and Evans, T.D., *Svensk Papperstidn.*, 88(6), R78 (1985).

141. Allison, R.W. and Graham, K.L., *J. Pulp Paper Sci.*, 16(1), J28 (1990).

142. Giust, W., McLellan, F. and Whiting, P., *J. Pulp Paper Sci.*, 17(3), J73 (1991).

143. Rapson, W.H., *Tappi*, 39(5), 284 (1956).

144. Lundqvist, M., *Svensk Papperstidn.*, 82(1), 16 (1979).

145. Sjogren, B. and Moldenius, S., Int. Symp. Wood Pulping Chem., Vol 2, 125 (1981).

146. Hobbs, G.C. and Abbot, J., *J. Pulp Paper Sci.*, (submitted 1992).

147. Hobbs, G.C. and Abbot, J., Int. Symp. Wood Pulping Chem., Vol 1, 579 (1991).

148. Janson, J. and Forsskahl, I., Int. Symp. Wood Pulping Chem., 603 (1989).

149. Pero, R.W. and Dence, C.W., *J. Pulp Paper Sci.*, 12(6), J192 (1986).

150. Farrington, A. and Mulcahy, J.P., *Appita*, 45(6), 389 (1992).

151. Gierer, J., Jansbo, K., Yang, E., Yoon, B. and Reitberger, T., Int. Symp. Wood Pulping Chem., Vol 1, 93 (1991).

152. Gierer, J., Jansbo, K. and Reitberger, T., Int. Symp. Wood Pulping Chem., Vol 2, 157 (1991).

153. Gierer, J., Yang, E. and Reitberger, T., Int. Symp. Wood Pulping Chem., Vol 2, 197 (1991).

154. Sjogren, B., Zachrison, H. and Reitberger, T., Int. Symp. Wood Pulping Chem., 161 (1989).

155. Tatsumi, K. and Terashima, N., *Mokuzai Gakkaishi*, 31(9), 761 (1985).

156. Tatsumi, K., Murayama, K. and Terashima, N., Tappi Int. Oxy. Delig. Conf., 99 (1987).

157. Barkhau, R., Bastian, J. and Thompson, N.S., *Tappi*, 68(10), 110 (1985).

158. Gierer, J. and Imsgard, F., *Svensk Papperstidn.*, 80(16), 510 (1977).

159. Basta, J., Holtinger, L. and Hook, J., Int. Symp. Wood Pulping Chem., Vol 1, 237 (1991).

160. Ali, T., Fairbank, M., McArthur, D., Evans, T.D. and Whiting, P., *J. Pulp Paper Sci.*, 14(2), J23 (1988).

161. Graham, M.D., Revol, J.F., Fairbank, M.G., Tay, C.H. and Whiting, P., *Cellulose Chem. Tech.*, 21, 371 (1987).

162. Fairbank, M.G., Colodette, J.L., Ali, T., McLellan, F. and Whiting, P., *J. Pulp Paper Sci.*, 15(4), J132 (1989).

163. Ali, T., Evans, T.D. and Fairbank, M.G., C.P.P.A. Ann. Mtg., B15 (1988).

164. Ali, T., Evans, T.D., Fairbank, M., McArthur, D. and Whiting, P., *J. Pulp Paper Sci.*, 16(6), J169 (1990).

165. Ali., T., Krull, U. and Whiting, P., C.P.P.A. Ann. Mtg., A99 (1990).

166. Kuczynski, K., Nijs, H. and May, B.H., *Tappi*, 75(8), 142 (1988).

167. Abbot, J. and Ginting, Y.A., *J. Pulp Paper Sci.*, 18(3), J85 (1992).

168. Smith, P.K. and McDonough, T.J., *Svensk Papperstidn.*, 88(12), R106 (1985).

169. Agnemo, R. and Gellerstedt, G., *Acta Chem. Scand.*, B33(5), 337 (1979).

170. Singley, J.E. and Black, A.P., *J. Am. Water Works Assoc.*, 1549 (1967).

171. Flynn, C.M., *Chem. Rev.*, 84, 31 (1984).

172. Sylva, R.N., *Rev. Pure Appl. Chem.*, 22, 115 (1972).

173. Danesi, P.R., Chiarizia, R., Scibona, G. and Riccardi, R., *Inorg. Chem.*, 12(9), 2089 (1973).

174. Murphy, P.J., Posner, A.M. and Quirk, J.P., *J. Colloid Int. Sci.*, 56(2), 298 (1976).

175. Murphy, P.J., Posner, A.M. and Quirk, J.P., *J. Colloid Int. Sci.*, 56(2), 270 (1976).

176. Melikhov, I.V., Kozlovskaya, E.D., Berliner, L.B. and Prokofiev, M.A., *J. Colloid Int. Sci.*, 117(1), 1 (1987).

177. Ohyabu, M. and Ujihira, Y., *J. Inorg. Nucl. Chem.*, 43, 1948 (1981).

178. Khoe, G.H., Brown, P.L., Sylva, R.N. and Robins, R.G., *J. Chem. Soc., Dalton Trans.*, 1901 (1986).

179. Abbot, J. and Brown, D.G., *Int. J. Chem. Kinet.*, 22, 963 (1990).

180. Krivorochko, O.P., Zolotovskii, B.P., Buyanov, R.A., Zaikovskii, V.I. and Sulima, G.E., *Kinet. Catal.*, 18, 169 (1977).

181. Wells, C.F. and Salam, M.A., *J. Inorg. Nucl. Chem.*, 31, 1083 (1969).

182. Ant-Wuorinen, O. and Visapaa, A., *Paperi ja Puu*, 47(9), 477 (1965).

183. Wells, C.F. and Salam, M.A., *J. Chem. Soc. A*, 24 (1967).

184. Brown, P.L., Sylva, R.N. and Ellis, J., *J. Chem. Soc., Dalton Trans.*, 723 (1985).

185. Einaga, H., *J. Chem. Soc., Dalton Trans.*, 912 (1977).

186. Einaga, H., *J. Inorg. Nucl. Chem.*, 43, 229 (1981).

187. Akitt, J.W. and Elders, J.M., *J. Chem. Soc., Dalton Trans.*, 1347 (1988).

188. Aveston, J., *J. Chem. Soc.*, 4438 (1965).

189. Brown, P.L., Sylva, R.N., Batley, G.E. and Ellis, J., *J. Chem. Soc., Dalton Trans.*, 1967 (1985).

190. Turner, R.C., *Can. J. Chem.*, 53(19), 2811 (1975).

191. Cordier, D.R. and Bixler, H.J., *Tappi*, 70(11), 99 (1987).

192. Aveston, J., *J. Chem. Soc.*, 4444 (1965).

193. Lagerstrom, G., *Acta Chem. Scand.*, 13, 722 (1959).

194. Bechtold, M.F., *J. Amer. Chem. Soc.*, 59, 532 (1955).

195. Greenberg, S.A., *J. Amer. Chem. Soc.*, 62, 6508 (1958).

196. Greenberg, S.A., *J. Chem. Ed.*, 36(5), 218 (1959).

197. Greenberg, S.A. and Sinclair, D., *J. Amer. Chem. Soc.*, 59, 435 (1955).

198. Greenberg, S.A., *J. Polymer Sci.*, 27, 523 (1958).

199. Mizutani, T., Fukkshima, Y. and Kamigaito, O., *Bull. Chem. Soc. Jpn.*, 63(2), 618 (1990).

200. Pokric, B. and Pucar, Z., *J. Inorg. Nucl. Chem.*, 33, 445 (1971).

201. Matijevic, E., Couch , J.P. and Kerker, M., *J. Phys. Chem.*, 66, 111 (1962).

202. Schorsch, G., *Bull. Soc. Chim. France*, 4, 985 (1965).

203. Schorsch, G., *Bull. Soc. Chim. France*, 4, 988 (1965).

204. Sylva, R.N. and Davidson, M.R., *J. Chem. Soc., Dalton Trans.*, 232 (1979).

205. Perrin, D.D., *J. Chem. Soc.*, 3189 (1960).

206. Colodette, J.L., "Factors Affecting Hydrogen Peroxide Stability in the Brightening of Mechanical and Chemimechanical Pulps", Ph.D. Thesis, SUNY College of Environmental Science and Forestry, 1987.

207. Baes, C.F. and Mesmer, R.E., "The Hydrolysis of Cations", John Wiley, New York, 1976.

208. West, T.S., *Ind. Chem.*, April, 191 (1961).

209. West, T.S., *Ind. Chem.*, May, 241 (1961).

210. West, T.S., *Ind. Chem.*, June, 295 (1961).

211. Taylor, R.M., *Clay Miner.*, 19, 591 (1984).

212. Hansen, H.C.B. and Taylor, R.M., *Clay Miner.*, 25, 161 (1990).

213. Harder, H., *Clay Miner.*, 12, 281 (1977).

214. Plotnikov, V.I. and Safonov, I.I., *Dokl. Acad. Nauk. SSSR*, 244(5), 1174 (1979) ; *Chem. Abstr.* 90:175420.

215. Novikov, A.I. and Rakhmonberdyev, A., *Soosazhdenie Gidroksidami*, 2, 28 (1977) ; *Chem. Abstr.* 91:112921.

216. Plotnikov, V.I., Safonov, I.I. and Efremenkov, V.M., *Vestn. Akad. Nauk. Kaz. SSR*, 5:28 (1983) ; *Chem. Abstr.* 99:28825.

217. Margulis, E.V., Brigadnova, V.V. and Strunnikova, N.A., *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, 3, 54 (1988) ; *Chem. Abstr.* 109:194320.

218. Yakubov, K.M., Chernakova, E.Y., Kvyatkovskaya, I.V., Kalontarova, E.Y. and Sakhibova, L.Z., *Zh. Neorg. Khim.*, 30(4), 944 (1985) ; *Chem. Abstr.* 102:210188.

219. Plotnikov, V.I., Safonov, I.I. and Efremenkov, V.M., *Vestn. Akad. Nauk Kaz. SSR*, 11, 32 (1982) ; *Chem. Abstr.* 98:100221.

220. Zheng-Yuan, D. and Mao-Rong, S., Int. Symp. Wood Pulping Chem., poster sessions, 367 (1989).

221. Abbot, J. and Wright, P.J., *Appita*, 45(5), 332 (1992).

222. Allison, R.W. and Graham, K.L., *J. Pulp Paper Sci.*, 15(4), J145 (1989).

223. Hobbs, G.C., " Investigation of the role of peroxide radical species in the bleaching of mechanical pulp" , Ph.D. Thesis, University of Tasmania, 1993.

224. Glasser, W.G., "Lignin", pp 51-61, in "Pulp and Paper, Chemistry and Chemical Technology", 3rd Ed, Vol 1, Casey, J.P. Editor, Wiley-Interscience, New York, 1980.

225. Gellerstedt, G., Hardell, H.-L. and Lindfors, E.-L., *Acta Chem. Scand.*, B34, 669 (1980).

226. Holmbom, B., Ekman, R., Sjoholm, R., Eckerman, C. and Thornton, J., *Das Papier*, 45(10), V16 (1991).
227. Wieber, J., Kulik, F., Pethica, B.A. and Zuman, P., *Colloids Surfaces*, 33, 141 (1988).
228. Samuelson, O. and Stolpe, L., *Svensk Papperstidn.*, 74(18), 545 (1971).
229. Croon, I. and Andrews, D.H., *Tappi*, 54(11), 1893 (1971).
230. Lachenal, D. and Papadopoulos, J., Int. Symp. Wood Pulp. Chem., 295 (1987).
231. Gellerstedt, G. and Agnemo, R., *Acta Chem. Scand.*, B34(4), 275 (1980).
232. Defaye, J. and Gadelle, A., *Pulp Paper Can.*, 75(11), T394 (1974).
233. Manouchehri, M. and Samuelson, O., *Svensk Papperstidn.*, 76(13), 486 (1973).
234. Tan, S.S.H. and Balazs, M.K., *Semiconductor Int.*, 11(12), 100 (1988).
235. Reichert, J.S., McNeight, S.A. and Rudel, H.W., *Ind. Eng. Chem., Anal. Ed.*, 11(4), 194 (1939).
236. Kraft, F., p724 in "Pulp and Paper Manufacture", 2nd Ed., Vol 1, McDonald, R. G. Editor, McGraw-Hill Book Company, New York, 1967.

APPENDIX A

Publications

This article has been removed for copyright or proprietary reasons.

Abbot, J Brown, D.G, (1990) inetics of iron cataly ed decomposition of hydrogen peroxide in alkaline solution, nternational ournal of chemical kinetics, 9, 963 9 4

John Abbot, Douglas G. Brown (1990) tabili ation of iron catalysed hydrogen peroxide decomposition by magnesium, anadian Journal of hemistry, 6 (9), 1 3 1 43

John Abbot, Douglas G. Brown (1990) The influence of magnesium and other additives on iron catalysed decomposition of alkaline hydrogen peroxide, Appita, 43(6)

John Abbot, Douglas G. Brown, (1989), The influence of additives on transition metal catalysed decomposition of alkaline hydrogen peroxide, 6th ISWPC/89